



CF3NO photodissociation dynamics

M. P. Roellig, P. L. Houston, M. Asscher, and Y. Haas

Citation: The Journal of Chemical Physics **73**, 5081 (1980); doi: 10.1063/1.439986 View online: http://dx.doi.org/10.1063/1.439986 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/73/10?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

A theory for the photodissociation of polyatomic molecules, with application to CF3I J. Chem. Phys. **84**, 4288 (1986); 10.1063/1.450051

Photodissociation dynamics of 1,3,5triazine J. Chem. Phys. **81**, 4517 (1984); 10.1063/1.447421

Stateselective photodissociation dynamics of CF3NO J. Chem. Phys. **76**, 3339 (1982); 10.1063/1.443333

Twophoton excitation as a monitoring technique for photodissociation dynamics: CF3NO \rightarrow CF3+NO(v,J) J. Chem. Phys. **72**, 768 (1980); 10.1063/1.438914

Latetime gain of the CF3 I iodine photodissociation laser J. Appl. Phys. **45**, 2174 (1974); 10.1063/1.1663565



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 128.59.226.54 On: Tue, 09 Dec 2014 22:59:16

CF₃NO photodissociation dynamics

M. P. Roellig^{a)} and P. L. Houston^{b)}

Department of Chemistry, Cornell University, Ithaca, New York 14850

M. Asscher and Y. Haas

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel (Received 6 June 1980; accepted 1 August 1980)

The predissociation of CF₃NO from 600–680 nm has been studied by monitoring the nascent NO product in real time using a two-photon laser excited fluorescence (TPEF) technique. The observation that the rate of production of NO is equal to the rate of decay of excited CF₃NO indicates that no long-lived intermediate is involved in the dissociation. Detection of NO(v'' = 3) following 600 nm dissociation sets an upper limit of 33 kcal/mole on the C–N bond dissociation energy. The nascent vibrational and rotational distributions estimated from the observed TPEF spectra establish that greater than 95% of the NO product is formed in its ground vibrational state and that all vibrational states are rotationally excited. The rotational excitation is discussed in terms of the dynamics of the dissociation. Possible predissociation mechanisms are considered.

I. INTRODUCTION

Predissociating molecules appear to be an ideal substrate for exploring state selective photochemistry.¹ They are characterized by a structured, well defined absorption spectrum on the one hand and by a direct, unimolecular dissociation channel on the other hand. That these properties can be used in practical applications has been demonstrated by recent studies of photochemical isotope separation² in such molecules as formaldehyde^{3,4} and s-tetrazine.^{5,6} However, these properties also make it possible to obtain fundamental dynamical information, particularly for those systems which can be probed using laser excitation. Recent examples include H_2CO , ⁷⁻⁹ glyoxal, ¹⁰⁻¹⁷ cyclobutanone, ¹⁸ s-tetra-zine, ¹⁹ NH₃, ²⁰ HNCO, ²¹ and a variety of van der Waal's complexes. ²² In most of these cases the dissociation dynamics have been monitored either by observing lifetimes and fluorescence quantum yields as a function of excitation wavelength or by observing product state distributions at a fixed excitation wavelength. Only a few studies have combined detailed probing of product state distributions with tunable excitation (e.g., Ref. 23). In this paper the predissociation of CF₃NO has been examined by measuring the appearance time, quantum yield, and energy distribution of the NO product as functions of dissociation wavelength. The results offer insights into the dynamics of the dissociation and into the predissociation mechanism.

 CF_3NO is a stable, blue gas with a weakly structured absorption spectrum²⁴ whose origin near 716 nm²⁵ lies well above the dissociation limit for ground state CF_3NO . Predissociation of CF_3NO has been studied previously by monitoring fluorescence lifetimes in low pressure gas samples²⁶ and in low temperature matrices.²⁵ The lifetimes were found to be much shorter than that of 36 μ sec calculated from the integrated absorption coefficient²⁷ and decreased from a value of 285 nsec at the origin²⁵ to values of 19 nsec at 665 nm and 0.2 nsec at 550 nm.²⁶ We have recently shown that infrared fluorescence²⁸ and two-photon laser excited fluorescence $(TPEF)^{29}$ can be used to monitor the nascent NO product following visible laser photolysis of CF₃NO. The latter technique has several advantages. First, it can monitor individual NO vibrational, rotational, and electronic levels, including the ground level. This advantage is significant since it is found that NO(v = 0) is the dominant vibrational level populated by dissociation at all wavelengths used in this study. Second, the TPEF method has a higher sensitivity than does the infrared fluorescence technique. Finally, the time resolution of roughly 5 nsec makes it possible to monitor directly the appearance time of the NO product.

II. EXPERIMENTAL

The nascent NO product of CF₃NO photolysis was detected by a two-photon laser excited fluorescence (TPEF) technique described briefly in a previous publication.²⁹ A detailed schematic of the experimental apparatus is shown in Fig. 1. Two pulsed dye lasers (Quanta-Ray, PDL-1), each pumped by a separate Nd:YAG laser, were used for these experiments. The first YAG laser (Quanta-Ray, DCR-1) pumped a "red" dye laser which was tuned between 600 and 670 nm to dissociate CF₃NO via its $n - \pi^*$ transition. This laser produced pulses of roughly 5 nsec (FWHM) duration with energies of 5-35 mJ, depending on the wavelength. Its linewidth was approximately 0.5 cm⁻¹. The second YAG laser (Quanta-Ray, DCR-1A) pumped a "blue" dye laser which was tuned between 450 and 500 nm to excite the NO dissociation fragment to its $A^{2}\Sigma^{+}$ state via a twophoton transition. It produced roughly 2-4 mJ/pulse. The two dye laser beams were propagated colinearly in opposite directions through the sample cell and were each focused to the same spot by a 5 in. focal length lens. Fluorescence from NO($A^{2}\Sigma^{*}$) was collected by a 10 cm focal length mirror and focused through a filter (Corning, 7-54) onto a solar-blind photomultiplier tube (Hamamatsu, R166UH). Different excited states of CF₃NO were prepared by varying the wavelength of the red laser, while different internal states of the NO product were probed by varying the wavelength of the blue laser. Signals were averaged by a boxcar inte-

^{a)}American Chemical Society-Petroleum Research Fund Fellow.

b)Alfred P. Sloan Research Fellow.

TWO PHOTON EXCITATION OF NASCENT PHOTODISSOCIATION





grator (PAR, 162/164) and displayed on one channel of a two-pen chart recorder. The power of the blue dye laser was monitored by a 4% reflection into a thermopile (Eppley) and recorded on the second channel of the twopen chart recorder. Because the optimal alignment of the two lasers would have caused each laser to propagate into the cavity of the other laser, filters (Corning 5-56 and Schott RG495) were used to prevent the red and blue beams from entering the cavity of the alternate laser.

The timing of the two laser pulses was controlled by a clock and delay circuit. The first output pulse from this circuit simultaneously triggered the flashlamps of the two YAG lasers at a 10 Hz repetition rate. A second pulse, delayed by ~ 250 $\mu\,sec$ from the first, triggered a fast delay generator (Evans, 4141-1) which produced two pulses, a reference pulse (REF), and a delayed pulse (DEL), separated by 0-10000 nsec with < 5 nsec jitter. For experiments in which the delay time between the laser pulses was held constant, the REF and DEL pulses were used to trigger the Q switches of the YAG lasers pumping the red and blue dye lasers, respectively. The actual timing of the two dye laser pulses was monitored by two identical photodiodes (Hewlett Packard, 5082-4220) placed on either side of the photolysis cell. The jitter between the output pulses was less than 5 nsec. For experiments in which the delay time between the laser pulses was scanned continuously, the DEL pulse was used to trigger the YAG laser pumping the red dye laser, while the REF signal was used to trigger a boxcar integrator (PAR, 160) which was used simply as a variable delay generator. The gate output from this boxcar triggered the YAG laser pumping the blue dye laser. As the gate was scanned in time, the blue laser was triggered at successively longer delays relative to the red laser. The scan rate of the signal recording boxcar (PAR, 162/164) was set to match the scan rate of the triggering gate. Thus, the total integrated fluorescence from the NO fragment was still monitored, but it was probed at continuously variable delays with respect to the photolysis pulse from the red laser.

Flowing CF₃NO samples were always used when NO(v = 0) excitation spectra were recorded by TPEF. This precaution was necessary because some NO(v = 0) from previous photolysis pulses always remained in the cell when static samples were used. The background signal due to prior photolysis was determined to be negligible when the flow system was used. Some background NO signal was also caused by dissociation of CF₃NO by the blue dye laser. However, this background was determined to be < 5% of the total intensity for any rotational line in the NO spectrum.

For standardization purposes the two-photon laser induced fluorescence spectrum of pure NO at room temperature was recorded using only the blue laser in conjunction with the fluorescence collection and detection apparatus described above.

Trifluoronitrosomethane (PCR, Inc.) was pumped on at 77 °K to remove NO and was distilled from a pentane slush bath (143 °K) to remove decomposition products. Nitric oxide (Matheson) was purified by trap to trap distillation at 77 °K. Photolysis of CF₃NO was performed both on static and on flowing samples. A flow system similar to that used here has been described elsewhere.²⁸ However, since different cells were employed, the flow rates were somewhat slower. Cell pressures were monitored with a capacitance manometer (MKS, model 221, 221A, or Trutorr).

III. RESULTS

A. Vibrational energy of the NO fragment

Figure 2 presents the raw data obtained from the TPEF technique following dissociation of CF₃NO at 600 nm. The bands marked a and b are due to transitions from the ${}^{2}\Pi_{3/2}$ spin component of the NO(X) state, which lies 124.2 cm⁻¹ above the ${}^{2}\Pi_{1/2}$ component. The latter gives rise to the bands marked c and d. Extensive rotational excitation prevents a simple estimate of the relative vibrational populations. In order to determine these populations more accurately, an excess of argon was used to ensure complete rotational and electronic $({}^{2}\Pi_{3/2} - {}^{2}\Pi_{1/2})$ relaxation. Under these conditions the intensity of the v'' = v - v' = 0, $O_{21} + P_{11}$ band head of the ${}^{2}\Pi_{1/2}$ transition, labeled d in the figure, was taken as a measure of the total population for each v'' = v level. The relative intensities were corrected for the Franck-Condon factors³⁰ and for the difference in probe laser intensity at the wavelengths employed. In preliminary



FIG. 2. TPEF spectra of nascent NO(v''=0, 1, and 2) produced by photolysis of CF₃NO at 600 nm. The transitions monitored are identified by the energy level diagram at the left. The intensity scale is different for each of the three spectra.



FIG. 3. Relative populations of NO (v''=0) and NO (v''=1) as a function of dissociation wavelength. Figure 3(a) (upper) shows the variation in v''=0 yield, while Fig. 3(b) (lower) displays the variation in the (v''=1)/(v''=0) ratio. The dashed line and the right-hand ordinate in Fig. 3(b) give the ratio expected on statistical grounds.

experiments it was found that the NO TPEF signal varied as the 1.3 power of the (blue) probe laser intensity. In determining the vibrational distribution for 600 nm photolysis, a sample of 0.4 Torr CF₃NO in 102 Torr of argon was irradiated, and the probe laser pulse was delayed by 80 nsec with respect to the photolysis pulse. As discussed in Sec. IVC.1, this delay is too short to allow appreciable vibrational energy transfer. The relative populations in the v'' = 0, 1, 2, and 3 levels were determined to be 1.0:0.03:0.01:0.003. Due to signal-tonoise considerations and uncertainties introduced by the correction procedure, these numbers are probably accurate only to within 50%. Population of the v''=4 level was probed by attempting to detect TPEF after excitation of the v'' = 4 - v' = 1 transition; no signal was observed. The Franck-Condon factor and the laser intensity used for this measurement place an upper limit of 0.0007 on the (v'' = 4)/(v'' = 0) population ratio.

The relative quantum yields of NO(v = 0) and NO(v = 1)were measured point by point at several CF₃NO photolysis wavelengths between 600 and 670 nm. The delay time between the photolysis and probe laser pulses was 10-20 nsec, while the sample pressure was 0.10 Torr of CF₃NO in 100 Torr of argon. The results, which are corrected for the wavelength variations of CF₃NO absorption coefficient and photolysis laser intensity, are displayed in Figs. 3(a) and 3(b). The ordinate of these figures requires some explanation. The quantum yield



FIG. 4. Excitation spectrum for the $v'' = 1 \rightarrow v' = 0$, O_{12} branch of (a) pure NO at room temperature and (b) NO(v'' = 1) product of 600 nm photodissociation of CF₃NO.

of NO(v = 0) was roughly constant with photolysis wavelength; its average was set to 1.0 for reasons to be discussed in Sec. IV B. The quantum yield of NO(v = 1) relative to NO(v = 0) was then determined as described above and found to decrease with increasing wavelength as shown in Fig. 3(b). The dashed line in the figure will be discussed in Sec. IV C.1. NO(v = 1) infrared fluorescence²⁸ was also measured as a function of excitation wavelength and found to give results similar to those presented here.³²

B. Rotational energy of the NO fragment

The rotational energy distribution of the NO(${}^{2}\Pi_{3/2}$) fragment was measured using the two-photon laser induced fluorescence technique following photolysis of CF₃NO at wavelengths of 670, 640, and 600 nm. The CF_3NO pressure was 0.1-0.3 Torr, while the delay time between photolysis and probe pulses was 10-20 nsec. The O_{12} branch, marked a in Fig. 2, was chosen for estimating the extent of rotational excitation since this branch is well separated from other branches and since single rotational lines are easily assigned. The excitation spectra for the v'' + v' = 0 + 0, O_{12} branch, published as Fig. 1 of Ref. 29, employed a photolysis wavelength of 670 nm and a CF₃NO pressure of 0.1 Torr. The excitation spectrum for the $v'' \rightarrow v' = 1 \rightarrow 0$, O_{12} branch, shown here in Fig. 4, employed a photolysis wavelength of 600 nm and a CF₃NO pressure of 0.27 Torr. Figure 4(b) displays the spectrum of the nascent

NO fragment from the CF₃NO photolysis, while Fig. 4(a) shows that obtained from 10 Torr of pure NO at room temperature. For the v'' + v' = 1 + 0 spectrum of Fig. 4, as well as for the v'' + v' = 0 + 0 spectrum of Ref. 29, the relative population of the J'' = 8.5 - 15.5 levels of the NO dissociation fragment is much greater than the population of the same J'' levels in pure NO at room temperature.

C. Electronic energy of the NO fragment

Spin relaxation rates $({}^{2}\Pi_{3/2} \rightarrow {}^{2}\Pi_{1/2})$ in NO at room temperature are almost gas kinetic, ³¹ so that estimates of the extent of electronic excitation in the ${}^{2}\Pi_{3/2}$ component must be made at very low pressures. Even under these conditions, however, the overlap of rotational lines and the possibility that different electronic states have different rotational distributions prevent any quantitative comparison between the population of the two spin components. Qualitatively, however, our data suggest that the electronic distribution may be dependent on photolysis wavelength. The complete TPEF spectra of NO(v'' = 0) following photolysis of CF₃NO at 600 and 670 nm are shown in Figs. 5(a) and 5(b), respectively. The change from 600 to 670 nm in the intensity ratio between the O_{12} or $O_{22} + P_{12}$ band head of the ${}^{2}\Pi_{3/2}$ state compared to the O_{11} or $O_{21} + P_{11}$ band head of the ${}^{2}\Pi_{1/2}$ state suggests that the population of the upper ${}^{2}\Pi_{3/2}$ state increases with decreasing dissociation wavelength.



FIG. 5. Complete two-photon excitation spectrum of NO(v''=0) produced by (a) 600 nm and (b) 670 nm dissociation of CF₃NO.



FIG. 6. Appearance time of the NO (v'' = 0) TPEF signal at two photolysis wavelengths.

D. Appearance time of the NO fragment

The appearance time of NO(v = 0) was measured by varying the time delay between the dissociation and probe laser pulses. Because v = 0 is the most populated level of the NO product, the $O_{21} + P_{11}$ band head was probed on the X(v''=0) - A(v'=0) transition. Figure 6 displays the time dependence of the NO concentrations observed following photolysis of 0.11 Torr of flowing CF_3NO at 670 and 600 nm. These signals, as well as a similar one taken at 650 nm, each display an exponential rise with the respective time constant listed in Table I. The comparison of these time constants with the CF₃NO fluorescence decay times will be discussed below.

IV. DISCUSSION

A. The TPEF technique

The use of TPEF for the quantitative measurement of product yields depends on two assumptions: (i) that the quantum yield of excited product fluorescence does not depend on the excitation wavelength, and (ii) that the relative intensities of rovibrational lines for a given electronic transition can be obtained from the Franck-Condon factors and the populations of the lower level involved in the transition. The first assumption is certainly valid under the experimental conditions employed for our experiments. Excitation was always to the NOA(v = 0) state, for which the fluorescence properties are well known. 33,34 The quantum yield for fluorescence is essentially unity at the low pressures used in this experiment. However, the efficient quenching of NOA(v'= 0) by CF_3NO , measured in separate experiments to proceed at $k_0 = 2.2 \times 10^7 \text{ sec}^{-1} \text{ Torr}^{-1}$, introduced small but strainghtforward corrections when comparing spectra taken at slightly different CF₃NO pressures.

The second assumption is less well founded since the two-photon cross sections are known to depend on polarization³⁵ and since the relative intensities of different rotational transitions may not be related to populations in a straightforward manner. However, it has been found previously that the known Franck-Condon factors³⁰ for the X(v''=0) - A(v'=0-3) transitions account reasonably well for the relative intensities of the TPEF bands.³⁶ The dependence of relative intensity on rotational population was checked by simulating the $X(v''=0) \rightarrow A(v'=0)$ TPEF spectrum of room temperature NO. The method, described below in Sec. IV C. 2, gave good agreement with experiment. In summary, it appears likely that assumptions (i) and (ii) are both valid under the conditions used for our experiments.

B. Dissociation mechanism

Our results strongly support the hypothesis that the NO fragment arises from predissociation from the S_1 state of CF₃NO. If dissociation were due to absorption to an underlying continuum, then the rise time of the NO product would be expected to be much more rapid than that observed in our experiments. Further evidence presented elsewhere³² comes from the comparison of the wavelength dependence of NO(v = 1) yield with the excitation spectrum of S_1 fluorescence. These two spectra are structurely similar in the region from 654-678 nm.

Our data also exclude the involvement of a long-lived intermediate in the predissociation. Consider the dissociation mechanism

$$CF_2NO \xrightarrow{h\nu} CF_2NO^*$$
 (1)

$$CF_3NO^* \xrightarrow{k_{diss}} CF_3 + NO$$
, (2)

where radiative and collisional quenching are assumed to be negligible. The time dependent changes in NO concentration are given by

$$d[\mathrm{NO}]/dt = k_{\mathrm{diss}}[\mathrm{CF}_{3}\mathrm{NO}^{*}] , \qquad (3)$$

whereas the concentration of CF_3NO^* at any time t following the excitation pulse is given by conservation of matter:

$$[CF_{3}NO^{*}]_{t} = [CF_{3}NO^{*}]_{0} - [NO]_{t} .$$
(4)

Equations (3) and (4) have the following solution:

.

$$[NO]_{t} = [CF_{3}NO^{*}]_{0} [1 - \exp(-k_{diss} t)], \qquad (5)$$

$$[CF_{3}NO^{*}]_{t} = [CF_{3}NO^{*}]_{0} \exp(-k_{diss}t) .$$
(6)

Thus, the decay time of the excited CF₃NO and the ap-

TABLE I. Comparison between NO appearance time and CF₃NO lifetime.

Excitation wavelength	670 nm	665 nm	650 nm	600 nm
NO appearance	18.1		· · · · · ·	
time (nsec)	19	•••	8,8	4.3 ^a
CF ₃ NO lifetime ^b	•••	19	10	3.2

^aThe time resolution of experiment was equal to the observed appearance time.

^bFrom Ref. 26.

pearance time of the NO fragment should be identical. Table I compares the appearance time data of Sec. III D with the CF₃NO^{*} lifetime data measured by Spears and Hoffland.²⁶ If a long-lived intermediate were involved in the dissociation, then the appearance time of the NO fragment would be longer than the decay time of S_1 CF₃NO. The good correlation of lifetimes shown in Table I rules out this possibility, although it should be noted that the agreement for $\lambda = 600$ nm may be fortuitous since the time resolution of our experiments was equal to the measured NO appearance time in this case.

Data on the wavelength dependence of the NO(v = 0) and NO(v = 1) quantum yields indicate that predissociation is likely to be the major decay channel for excited CF₃NO. The likelihood of this assertion is shown by considering the counterassumption. We suppose the existence of an alternative nonradiative decay channel which does not lead to dissociation. Let the nonradiative decay rate for this channel be k'. Then the total nonradiative rate is $(k' + k_{diss})$ and the total quantum yield for NO is $k_{diss}/(k'+k_{diss})$. Summation of the quantum yields for NO(v = 0) and NO(v = 1) in Fig. 3 shows that the total quantum yield of NO is essentially constant with dissociation wavelength. However, it is known that the total nonradiative rate increases dramatically from 20 nsec⁻¹ at 670 nm to 3 nsec⁻¹ at 600 nm.²⁶ If $k_{diss}/(k' + k_{diss})$ is to remain constant while $(k' + k_{diss})$ changes by nearly an order of magnitude, then either $k_{diss} \gg k'$ or $k' \gg k_{diss}$ with k_{diss}/k' equal to a constant. It seems unlikely that the two different nonradiative decay rates would vary with wavelength in such a way as to keep k_{diss}/k' constant. Therefore, we conclude that $k_{diss} \gg k'$, or that predissociation is the major decay channel for excited CF₃NO.

The presently available data do not adequately determine the type of predissociation mechanism. Three possibilities are shown schematically in Fig. 7. Because potential energy curves are not available for CF_3NO , those shown in Fig. 7 are based on calcuated curves for the similar HNO molecule.³⁷⁻⁴⁰ The loca-



FIG. 7. Possible CF₃NO predissociation mechanisms.

TABLE II. Parameters describing vibrational predissociation.

s	$E_0 ({\rm cm}^{-1})$	$A (\text{sec}^{-1})$
12	225	7.9×10^{8}
11	244	7.8 $\times 10^{8}$
10	266	$7.7 imes10^8$
9	293	7.6×10^{8}
8	325	7.5×10^{8}
7	365	7.3×10^{8}
6	417	7.0×10^{8}
5	485	6.7×10^{8}
4	580	6.3×10^{8}
3	716	5.7×10^{8}
2	913	4.7×10^{8}
•••		

tions and heights of the barriers on the S_1 and T_1 curves are highly speculative.

The highest energy dissociation pathway shown in Fig. 7 involves vibrational predissociation. If dissociation takes place by this route, then the lifetime of the initially excited state should be determined by the rate of energy redistribution on the S_1 surface. The appearance rate of the NO fragment should increase with increasing energy in accordance with the statistical formulations of unimolecular dissociation. This increase is indeed observed (Table I), but a simple calculation indicates that the magnitude of the increase is not easily accounted for by RRK theory. The unimolecular rate constant k_{diss} may be written as

$$k_{diss}(E) = A \left[(E - E_0) / E \right]^{s-1} , \qquad (7)$$

where E is the energy above the zero point energy level (on the S_1 surface), E_0 is the barrier height above the zero point energy level, and s is the effective number of oscillators. By using Eq. (7) one can obtain the dissociation rate constant ratio which should be observed when comparing two different excitation wavelengths. The equation fits the experimental data obtained for dissociation rates at 600 and 670 nm (Table I) only for the choices of s, E_0 , and A shown in Table II. Although the barrier heights seem reasonable, the values of A are certainly much too low to be realistic. We conclude, therefore, either that the RRK theory is not appropriate or that vibrational predissociation on the S_1 surface is not consistent with the experimental data.

The intermediate energy pathway in Fig. 7 corresponds to dissociation by tunneling through a barrier. As the excitation energy increases, it is expected that tunneling will become more rapid and that the rate of dissociation will increase. Although an increase in dissociation rate with increasing excitation energy is observed (Table I), an order of magnitude tunneling calculation predicts a physically unrealistic barrier when an asymmetrical Eckhart potential is used as a model. The notation employed for the following discussion is that of Johnston.⁴¹ The Eckhart potential is described by the barrier to dissociation V_1 , the second derivative of the potential at its maximum F^* , and the barrier V_2 to the reverse association reaction. Assuming the origin of the CF₃NO S₁ transition to be at 720 nm and the CF₃-NO bond dissocia-

J. Chem. Phys., Vol. 73, No. 10, 15 November 1980

TABLE III.	Tunneling	parameters
------------	-----------	------------

V ₁ (cm ⁻¹)	$\alpha_1^{\mathbf{a}}$	Predicted ^a k _{diss} (600 nm)/k _{diss} (670 nm		
20 000	10.4	35		
40 000	8.8	12		
80 000	8.0	7.9		
100 000	7.7	7.1		
200 000	7.1	6.0		
300 000	6.9	5.7		

^aChosen to give κ (600 nm) $\simeq 4 \times 10^{-6}$.

tion energy to be 33 kcal/mole, one obtains the relationship $V_2 \simeq V_1 + 2334$ cm⁻¹. The probability of tunneling at each encounter with the barrier is given by the transmission coefficient $\kappa(E)$. Calculations of $\kappa(E)$ were made using Eqs. (2-15) through (2-22) of Ref. 41 suitably corrected for the errata listed by Garrett and Truhlar.⁴² The results are expressed in terms of V_1 and α_1 , where the latter quantity is related to F^* through Eqs. (2-15) and (2-16) of Ref. 41. For a given value of V_1 , smaller values of α_1 imply a narrower barrier. Since the vibrational frequency in the bound part of the CF_3NO potential will be on the order of 8×10^{13} sec⁻¹ for excitation at 600 nm, and since the dissociation rate at this wavelength is about $3 \times 10^8 \text{ sec}^{-1}$ (Table I), we require the transmission coefficient κ to be about 4×10^{-6} . Table III lists for various values of V_1 the values of α_1 which give $\kappa \simeq 4 \times 10^{-6}$ for excitation at 600 nm. The table also lists the predicted ratio of dissociation rates for 600 nm vs 670 nm dissociation. The observed ratio is about 6 (Table I). As can be seen from Table III, although several combinations of V_1 and α_1 give $\kappa(600 \text{ nm})$ = 4×10^{-6} , the simultaneous experimental requirement that $k_{diss}(600 \text{ nm})/k_{diss}(670 \text{ nm}) = 6$ implies an unreasonably high ($V_1 = 200\,000 \text{ cm}^{-1}$) and narrow ($\alpha_1 = 7.1$) barrier. We conclude, therefore, that tunneling is not likely to be the mechanism for CF₃NO predissociation.

The lowest energy pathway in Fig. 7 corresponds to a two-step dissociation involving S_0 or T_1 as intermediates:

$$CF_3NO(S_1) \rightarrow CF_3NO(S_0 \text{ or } T_1) , \qquad (8)$$

$$CF_3NO(S_0 \text{ or } T_1) \rightarrow CF_3 + NO$$
 (9)

In order for the NO appearance time to be no longer than the S_1 decay time, we require $k_9 > k_8$. The rate constant for the first step may be written as⁴³

$$k_8 = 2\pi V^2 \rho / h = \tau_{\rm nr}^{-1} , \qquad (10)$$

where V is the coupling matrix element between the two states and ρ is the density of levels in the acceptor state. $\tau_{\rm nr}$ is the nonradiative lifetime which, for our case, is nearly equal to the observed lifetime. Equation (10) may be used to calculate the strength of the coupling matrix element from the observed lifetimes and the calculated density of states. The latter quantity was obtained from the semiclassical expression⁴⁴

$$\rho(E) = \frac{E^{s-1}}{(s-1)! \, \Pi h \nu_i} \,\,, \tag{11}$$

where s is the number of oscillators and v_i (i = 1 to s) are their frequencies. This expression neglects the contribution from the zero point energy of the vibrations and provides a lower estimate to the level density. The energy available to the T_1 molecules at a given excitation wavelength was estimated by assuming that for CF_3NO the ratio of the energy difference between T_1 and S_0 to that between T_1 and S_1 is equal to the calculated ratio for CH₃NO.⁴⁵ The vibrational frequencies of $S_0 CF_3 NO^{46}$ were assumed not to change appreciably for the T_1 state. Equations (10) and (11) were used to calculate the required coupling matrix elements at excitation energies of 16670 cm^{-1} (600 nm) and 14920 cm^{-1} (670 nm), as summarized in Table IV. Although no calculation of the S_1 - S_0 or S_1 - T_1 coupling elements is available for CF₃NO, the values in Table IV are smaller than those used to explain the coupling in other $n-\pi^*$ systems such as formaldehyde. 47-49 We conclude that S_0 or T_1 could provide a dissipative manifold for $S_1 CF_3 NO$ and that predissociation might take place through an S_0 or T_1 intermediate. In either case the coupling between S_0 or T_1 and the continuum would have to be strong enough so that $k_9 > k_8$; if the triplet is involved, its barrier to dissociation must be small.

C. Energy distribution of the NO fragment

1. Vibrational energy

It is extremely unlikely that the vibrational distributions measured in Sec. IIIA are significantly relaxed from the nascent distributions. For these experiments, the two-photon probe pulse was delayed 80 nsec from the photolysis pulse, while the pressures of CF₃NO and argon were 0.4 and 102 Torr, respectively. The known rate of NO(v = 1) deactivation by CF₃NO²⁸ or argon⁵⁰ can be used to calculate a vibration-to-translation relaxation time of 10^{-3} or $>2.5 \times 10^{-2}$ sec, respectively. Since these times are substantially longer than the 10⁻⁷ sec pulse delay, it is clear that vibration-to-translation energy transfer could not have occurred during our measurement. Vibration-to-vibration energy transfer may also be ruled out. Assuming that all the CF₃NO in the beam is dissociated and that 4% of the NO product is in v = 1, then the known rate for $2NO(v = 1) \rightarrow NO(v = 2)$ + NO $(v = 0)^{50}$ can be used to calculate a vibration-to-vibration relaxation time of 500 μ sec. Since this relaxation time is also much longer than the delay time employed, we can safely conclude that the measured vibrational distribution is the nascent distribution.

Our observation of NO(v = 3) at a dissociation wavelength of 600 nm places an upper limit on the CF_3 -NO bond dissociation energy of 33 kcal/mole. Although the difference between the photon energy and the NO(v = 3)

TABLE IV. Calculated densities and coupling elements for CF₃NO.

Energy (cm ⁻¹)	τ _{obe} (sec)	ρ(S ₀) (cm)	ρ(T ₁) (cm)	V(S ₀) (cm ⁻¹)	V(T ₁) (cm ⁻¹)
16 670	3× 10 ⁻⁹	5.6×10^{5}	2.8×10 ²	5.6×10-5	$2,5 \times 10^{-3}$
14 920	2×10 ⁻⁸	1.7×10^{5}	2.2×10^{1}	3.9×10^{-5}	3.0×10^{-3}

J. Chem. Phys., Vol. 73, No. 10, 15 November 1980

	2014	22.59.16



FIG. 8. (a) Relative NO vibrational populations observed following 600 nm photodissociation of CF_3NO . The solid line gives the observed vibrational distribution, while the dashed line gives the distribution expected on statistical grounds. (b) Vibrational surprisal as a function of the fraction of available energy which appears in the NO vibration.

energy is only 31 kcal/mole, analysis of the CF₃NO $n \rightarrow \pi^*$ spectrum suggests that absorption from hot vibrational modes having as much as 1.8 kcal/mole in energy may contribute to the dissociation. Our upper limit is in good agreement with the previously measured bond dissociation energy of 31 kcal/mole, ⁵¹ but is much lower than the recently reported value of 42 kcal/mole.⁵²

A surprisal analysis^{1,53} of the NO vibrational population shows that less NO(v'' = 1) but more NO(v'' = 2 and 3) is produced by the dissociation than would be expected on prior grounds. The prior distribution was determined by assuming equal probabilities for all product quantum states which are permitted by conservation of energy. The NO(v'' = v)/NO(v'' = 0) ratio is then given simply by the ratio $\rho(E, v)/\rho(E, 0)$, where $\rho(E, v)$ is the density of product states which have a total energy of E with vquanta in the NO vibration. Evaluation of $\rho(E, v)$ was performed by following the procedure outlined by Bogan

and Setser.⁵⁴ Equation (3) of Ref. 54 was integrated numerically using the known vibrational and rotational constants of NO⁵⁵ and the reported vibrational frequencies of CF_3 . ⁵⁶ A direct counting procedure was used to calculate the degeneracies and energies of the CF₃ levels, 57 while the available energy was calculated from the difference between the excitation energy and the bond dissociation energy.⁵¹ The resulting NO prior distributions are plotted as the dashed lines in Figs. 3(b) and 8(a). Figure 8(b) displays the surprisal $I = -\ln[P(v)/$ $P^{0}(v)$ as a function of the fraction of available energy appearing in the NO vibration. While more NO(v''=2)and NO(v'' = 3) is produced by the dissociation than would be expected on prior grounds, less NO(v'' = 1) is produced than expected at all dissociation wavelengths examined in this study. The surprisal for the NO(v'' = 1)/NO(v'' = 0) ratio is essentially constant as a function of dissociation wavelength. The nonlinear surprisal plot in Fig. 8(b) indicates that there is more than one constraint on the vibrational distribution of NO. This result is consistent with the coexistence of more than one dissociation mechanism, though it cannot be taken as proof. In the present case, dissociation on two different electronic surfaces, e.g., T_1 and S_0 , could possibly lead to two different vibrational distributions, each having a linear surprisal plot, whose sum gives the plot of Fig. 8(b). The limited number of v'' states observed precludes a meaningful deconvolution of this plot.

2. Rotational energy

It is likely that the rotational excitation spectra shown in Fig. 4(b) of this paper and in Fig. 1(b) of Ref. 29 probe the nascent rotational distribution from CF_3NO photolysis. At the CF_3NO pressure of 0.1-0.3 Torr used for these experiments there are \leq 1 hard sphere collisions in the delay time of 10-20 nsec between photolysis and probe pulses.

A qualitative evaluation of the rotational energy distribution can be made by comparing the excitation spectrum for the NO dissociation product in v'' = 1 or v'' = 0with that for pure NO at room temperature in v'' = 1 or v'' = 0 [i.e., by comparing Figs. 4(b) and 4(a) of this work or by comparing Figs. 1(b) and 1(a) of Ref. 29]. The fact that the product NO spectrum peaks at higher J'' than the pure NO spectrum in both cases indicates that the product NO rotational degrees of freedom are highly excited.

A quantitative evaluation of the rotational energy distribution has been performed by rotational contour analysis of the excitation spectra for the NO(v''=0) product from 600 and 670 nm CF₃NO photolysis and for the NO(v''=1) product from 600 nm photolysis. More accurate analyses could not be performed because of the overlap of rotational transitions within the O_{12} branch. It was assumed for simplicity that the nascent rotational distribution was Boltzmann and that each rotational transition has a Gaussian line shape. A simple computer program was written to simulate the O_{12} -branch twophoton excitation spectrum. The input parameters to the program were the Boltzmann temperature, the ground and excited state rotation constants, the zero



FIG. 9. Calculated and observed NO TPEF spectra showing rotational distribution of (a) pure NO (v''=1) formed by photolysis of CF₃NO at 600 nm. The calculated spectra assume Boltz-mann temperatures of 298 and 900°K, respectively.

point transition frequency, and the Gaussian linewidth. Rotational constants for NO were taken from Huber and Herzberg⁵⁵: $B_0'' = 1.69611 \text{ cm}^{-1}$, $B_1'' = 1.67854 \text{ cm}^{-1}$, and $B_0' = 1.98679 \text{ cm}^{-1}$. The transition frequencies are given by⁵⁸

$$\nu = \nu_0 + (15/4) B' - (4B' + B'') J'' + (B' + B'') J''^2 , \qquad (9)$$

where $\nu_0 = 44\,080.5$ or $\nu_0 = 42\,204.1$ cm⁻¹ is the frequency of the v'' - v' = 0 - 0 or 1 - 0 transition, respectively,⁵⁵ and B' and B'' are the rotational constants of the appropriate vibrational level in the ${}^{2}\Sigma^{+}$ and ${}^{2}\Pi_{3/2}$ states, respectively. Transition intensities were assumed to be simply proportional to a Boltzmann factor for the ground state population weighed by an average degeneracy of the ground and excited states:

$$I(J'') = (J' + J'' + 1) \exp[-B'' J'' (J'' + 1)/kT] .$$
 (10)

A Gaussian linewidth of 1.0 cm^{-1} was chosen to correspond roughly with the laser linewidth. The peak intensities of the observed spectra were then fit by varying the temperature. At a temperature of 298 °K the fits to the rotational intensities of the v'' + v' = 0 + 0 and 1 + 0 excitation spectra of pure NO were excellent; the former fit is shown in Fig. 9(a). The good agreement supports the validity of the method, as discussed in Sec. IV A.

For the NO(v'' = 1) product of CF₃NO photolysis at 600 nm, the Boltzmann distribution gave the best fit to the observed spectrum at a temperature of 900 °K. The calculated and observed spectra are displayed in Fig. 9(b). Calculated spectra with temperatures between 700 and 1100 °K did not give a noticeably better fit to the observed spectrum than did the calculated spectrum at 900 °K. The calculated spectral intensities show the largest discrepancies from the experimental intensities in the region where several rotational lines overlap. The calculated transition frequencies and, in particular, the degree of overlap in the band head region are very sensitive to the values chosen for B'' and B'. Thus, the largest errors are expected in this region. Fits similar to the ones shown in Fig. 9 were also obtained for the rotational distributions of NO(v''=0) produced by photolysis at 600, 640, and 670 nm. The best fits were obtained at the temperatures 1100 ± 200 , 1000 ± 200 , and 900±300°K, respectively. To within the error limits of our calculations, the rotational temperatures were the same for the NO(v''=0) fragments from CF₃NO dissociation at 600, 640, and 670 nm and for both the NO(v''=0) and NO(v''=1) fragments at 600 nm.

A simple calculation shows that conservation of angular momentum does not limit the amount of rotational excitation in the NO product. The required momentum can come either from the torque applied to the NO by the recoil of the fragments or from preparation of high CF₃NO torsional levels by the photolysis laser. We consider dissociation of CF₃NO at 670 nm, for which the NO(v'' = 0) excitation spectrum is fit by a Boltzmann distribution at a rotational temperature of 900 ± 300 °K. The average angular momentum for the NO fragment in this distribution is 14 \hbar . The assumption that all of this momentum comes from the fragment recoil would require that L, the angular momentum associated with the halfcollision between the CF_3 and NO fragments, be equal to at least 14 \hbar . The maximum value of L is $L_{\text{max}} = \mu v_{\text{max}} b$, where $\mu = 20.9$ amu is the reduced mass of the recoil fragments, $v_{\text{max}} = 2.2 \times 10^5 \text{ cm/sec}$ is the maximum recoil velocity consistent with conservation of energy at $\lambda_d = 670$ nm, and b is the impact parameter. The C-N-O equilibrium bond angle is 112.4° , while the equilibrium NO bond length is 1.198 Å.59 If the recoil takes place along the original C-N bond, then b = 0.64 Å and L_{max} $\simeq 45 \hbar$. It is evident that the recoil can provide more than enough angular momentum to cause the observed degree of NO rotational excitation. Alternately, angular momentum in the fragments could arise from excitation of high torsional levels of CF₃NO. The ground and excited states of CF₃NO have stable conformers in which the NO bond is eclipsed or staggered, respectively, with reference to the CF bonds. Electronic excitation therefore promotes torsional motion about the CN bond. The vibration-rotation energy available to the $S_1 CF_3 NO$ molecule is $> 1000 \text{ cm}^{-1}$ for dissociation at 670 nm, the longest wavelength investigated. If even 140 cm^{-1} of this energy were to excite the torsional modes, then the angular momentum of the NO torsion relative to the CF₃ would be sufficient to account for the observed rotation in the NO product fragment. Consequently, it appears that the angular momentum needed for rotational

excitation of the NO fragment can come either from the fragment recoil or from the torsional excitation of CF_3NO .

Less rotational energy appears in the NO fragment than would be expected on statistical grounds. The prior rotational distribution was calculated as $P^{0}(J) = \rho(E, v, J)/$ $\sum_{J} \rho(E, v, J)$. The density $\rho(E, v, J)$ was determined by omitting the summation over J in the rhs of Eq. (3) of Ref. 54 and proceeding as described above for the prior vibrational distribution. The prior rotational distributions were very nearly Boltzmann and had temperatures ranging from 1400 °K for the NO(v = 0) product of CF₃NO photolysis at 600 nm to 1025 °K for the NO(v = 0) product of photolysis at 670 nm. The prior rotational distribution for the NO(v = 1) product of 600 nm photolysis had a Boltzmann temperature of 1000 °K. In all cases these temperatures are somewhat higher than the Boltzmann temperatures which best fit the observed laser induced fluorescence spectra. However, the differences may not be significant due to the large error limits on the temperatures calculated by contour analysis.

3. Electronic energy

The small separation of the two spin components of the ground ²II state and the higher degeneracy of the upper one lead to a prior population ratio of about 1:1. Comparison between two-photon excitation spectra of the NO fragment produced by 600 and 670 nm photolysis of CF₃NO (Fig. 5) suggests that the NO electronic distribution changes with dissociation wavelength. The O_{12} and $O_{22} + P_{12}$ band heads of the ${}^{2}\Pi_{3/2}$ state are much more intense at 600 nm than at 670 nm so that the concentration of electronically excited NO appears to increase with decreasing photolysis wavelength. Since any variation in the rotational distribution with dissociation wavelength would also affect the relative intensities of the band heads, some caution must be used in making this interpretation. However, the preceding section has shown that the rotational distribution is rather insensitive to the photolysis wavelength over the range from 600-670 nm. It seems likely, therefore, that decreasing CF₃NO photolysis wavelengths favor production of the upper ${}^{2}\Pi_{3/2}$ component of the NO fragment.

V. CONCLUSION

The appearance time, quantum yield, and energy distribution for the NO product of CF_3NO photodissociation have been monitored as functions of dissociation wavelength. These studies show that the lifetime of excited CF_3NO is controlled by a rapid radiationless process which leads to dissociation. Although the exact mechanism of predissociation is not yet known, the most likely possibility involves the S_0 or T_1 state as an intermediate. Less rotational excitation and less NO(v = 1) are produced by the dissociation than would be expected on statistical grounds. On the other hand, more NO(v = 2)and NO(v = 3) is produced than expected. The nonlinear surprisal suggests the presence of more than one dissociation channel.

While much has been learned about the photophysics of the CF_3NO predissociation, a great deal of informa-

tion remains to be uncovered. In this study the energy distribution of the NO fragment has been probed as a function of dissociation wavelength but not specifically as a function of the state of CF_3NO which is excited. The latter study was precluded by the complicated nature of the room-temperature CF₃NO absorption spectrum. It would be interesting to know in particular how torsional excitation of CF_3NO^* affects the appearance time and rotational distribution of the NO product. The spectrum of CF₃NO cooled by expansion through a supersonic nozzle has recently been observed to show a very simple progression in the torsional mode.^{60,61} Therefore, it is likely that a study of CF₃NO photodissociation in a supersonic beam will provide answers to questions concerning the relationship between the initially excited state and the final product states. The pulsed nozzle source for such a study has recently been constructed in our laboratory. Other unanswered questions concern the partitioning of energy into the CF₃ internal degrees of freedom and into the relative translation between the CF_3 and NO fragments. Since less internal energy is found in the NO than would be expected on statistical grounds, more energy than expected must appear in the CF_3 fragment or in translation. The excitation appearing in the CF₃ fragment might be monitored by observing infrared fluorescence from this species, as has been done previously for the NO fragment of CF₃NO photolysis²⁸ and for the CH₃ and CH₂I fragments of CH₃I and CH₂I₂ photolysis.⁶² The translational energy distribution might be measured in a beam apparatus by timing the flight of the NO fragment from the location of dissociation to the location of detection. Finally, the appearance times of different NO vibrational levels might be monitored to establish whether they all come from the same potential energy surface. The accessibility of the CF_3NO absorption to powerful pulsed lasers and the possibilities for monitoring the final states of the dissociation products make this predissociative system an ideal candidate for further study.

ACKNOWLEDGMENTS

We would like to acknowledge several fruitful discussions with Professors E. R. Grant, R. D. Levine, and A. Ben Shaul concerning the vibrational distribution of the NO product. These experiments were performed in the Facility for Laser Spectroscopy in the Chemistry Department at Cornell University. We are grateful to the National Science Foundation for partial support of capital equipment in this facility and to the Exxon Corporation and the General Electric Company for partial support of operating expenses. The specific work reported here was supported by the Israel Commission for Basic Research and by the National Science Foundation under Grant Number CHE-76-21991. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

 ¹A. Ben-Shaul, Y. Haas, K. L. Kompa, and R. D. Levine, Lasers and Chemical Change (Springer, Berlin, 1980).
 ²Chemical and Biochemical Applications of Lasers, edited by V. S. Letokhov in C. B. Moore (Academic, New York, 1977), Vol. III.

- ³J. H. Clark, Y. Haas, P. L. Houston, and C. B. Moore, Chem. Phys. Lett. **35**, 82 (1975).
- ⁴J. B. Marling, J. Chem. Phys. **66**, 4200 (1977).
- ⁵R. R. Karl and K. K. Innes, Chem. Phys. Lett. **36**, 275 (1975).
- ⁶R. M. Hochstrasser and D. S. King, J. Am. Chem. Soc. 98,
- 5443 (1976).
 ⁷E. Yeung and C. B. Moore, J. Chem. Phys. 60, 2139 (1974);
 J. H. Clark, C. B. Moore, and N. S. Nogar, J. Chem. Phys. 68, 1264 (1978); J. C. Weisshaar, A. P. Baronavski, A. Cabello, and C. B. Moore, J. Chem. Phys. 69, 4720 (1978);
 J. Reiley, J. H. Clark, C. B. Moore, and G. Pimentel, J. Chem. Phys. 69, 4381 (1978); J. Weisshaar and C. B. Moore, J. Chem. Phys. 70, 5135 (1979).
- ⁸R. G. Miller and E. K. C. Lee, Chem. Phys. Lett. 33, 104 (1974); 41, 53 (1976); J. Chem. Phys. 68, 4448 (1978); K. Shibuya and E. K. C. Lee, J. Chem. Phys. 69, 5558 (1978); K. Y. Tang, P. W. Fairchild, and E. K. C. Lee, J. Phys. Chem. 83, 569 (1979).
- ⁹A. C. Luntz, J. Chem. Phys. 69, 3436 (1978).
- ¹⁰C. S. Parmenter, J. Chem. Phys. 41, 658 (1964); L. G. Anderson, C. S. Parmenter, and H. M. Polland, Chem. Phys. 1, 401 (1973); C. S. Parmenter and B. F. Rordorf, Chem. Phys. 27, 1 (1978).
- ¹¹J. T. Yardley, J. Chem. Phys. 56, 6192 (1972).
- ¹²G. Atkinson, R. A. McIlwain, and C. G. Venkatesh, J. Chem. Phys. 68, 726 (1978).
- ¹³H. G. Kuttner, J. L. Selzle, and E. W. Schlag, Chem. Phys. Lett. 48, 207 (1977); Chem. Phys. 28, 1 (1978).
- ¹⁴C. Michel and A. Tramer, Chem. Phys. 42, 315 (1979); B.
- Soep and A. Tramer, Chem. Phys. Lett. 64, 465 (1979). ¹⁵R. Naaman, D. M. Lubman, and R. N. Zare, J. Chem. Phys.
- 71, 4192 (1979).
- ¹⁶R. A. Beyer, P. F. Zittel, and W. C. Lineberger, J. Chem. Phys. 62, 4016 (1975); R. A. Beyer and W. C. Lineberger, J. Chem. Phys. 62, 4024 (1975); P. F. Zittel and W. C. Line-
- berger, J. Chem. Phys. 66, 2972 (1977).
- ¹⁷R. Van der Werf, E. Schutten, and J. Kommandern, Chem. Phys. **11**, 281 (1975).
- ¹⁸K. Y. Tang and E. K. C. Lee, J. Phys. Chem. **80**, 1833 (1976); E. K. C. Lee, Acc. Chem. Res. **10**, 319 (1977), and references therein.
- ¹⁹D. Coulter, D. Dows, H. Reisler, and C. Wittig, Chem. Phys. **32**, 429 (1978).
- ²⁰V. M. Donnelly, A. P. Baronavski, and J. R. McDonald, Chem. Phys. 43, 271 (1979).
- ²¹W. S. Drozdoski, A. P. Baronavski, and J. R. McDonald, Chem. Phys. Lett. 64, 421 (1979).
- ²²M. S. Kim, R. E. Smalley, L. Wharton, and D. H. Levy,
- J. Chem. Phys. 65, 1216 (1976); G. Kubiak, P. S. H. Fitch, L. Wharton, and D. H. Levy, J. Chem. Phys. 68, 4477
- (1978); K. E. Johnson, L. Wharton, and D. H. Levy, J.
- Chem. Phys. 69, 2719 (1978); W. Sharfin, K. E. Johnson, L. Wharton, and D. H. Levy, J. Chem. Phys. 71, 1292

(1979); J. E. Kenney, D. V. Brumbaugh, and D. H. Levy, J. Chem. Phys. 71, 4757 (1979).

- ²³P. L. Houston and C. B. Moore, J. Chem. Phys. 65, 757 (1976).
- ²⁴R. D. Gordon, S. C. Dass, J. R. Robins, H. F. Shurwell, and R. F. Whitlock, Can. J. Chem. **54**, 2658 (1976).
- ²⁵J. Goodman and L. Brus, J. Am. Chem. Soc. 100, 2971 (1978).
- ²⁶K. G. Spears and L. Hoffland, J. Chem. Phys. **66**, 1755 (1977).
- ²⁷J. Mason, J. Chem. Soc. 1957, 3904.

- ²⁸M. P. Roellig and P. L. Houston, Chem. Phys. Lett. 57, 75 (1978).
- ²⁹M. Asscher, Y. Haas, M. P. Roellig, and P. L. Houston, J. Chem. Phys. **72**, 768 (1980).
- ³⁰R. W. Nicholls, J. Res. Natl. Bur. Stand. (U.S.A) Sect. A 68, 535 (1964).
- ³¹Y. Nachshon and P. D. Coleman, J. Chem. Phys. **61**, 2523 (1974).
- ³²M. P. Roellig, Ph. D. Dissertation, Cornell University, 1980.
- ³³J. Brzozowski, P. Erman, and M. Lyyra, Phys. Scr. 14, 29 (1976); A. B. Callear and M. J. Pilling, Trans. Faraday Soc. 66, 1618, 1886 (1970).
- ³⁴H. Zacharias, J. B. Halpern, and K. H. Welge, Chem. Phys. Lett. 43, 41 (1976).
- ³⁵R. G. Bray and R. M. Hochstrasser, Mol. Phys. **31**, 1199 (1976).
- ³⁶M. Asscher and Y. Haas, Chem. Phys. Lett. **59**, 231 (1978).
- ³⁷P. A. Freedman, Chem. Phys. Lett. 44, 605 (1976).
- ³⁸A. A. Wu, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. Lett. **35**, 316 (1976).
- ³⁹A. W. Salloto and L. Burnelle, Chem. Phys. Lett. **3**, 80 (1969).
- ⁴⁰O. Nomura and S. Iwath, Chem. Phys. Lett. 66, 523 (1979).
- ⁴¹H. S. Johnston, Gas Phase Reaction Rate Theory (Ronald, New York, 1966).
- ⁴²B. C. Garrett and D. G. Truhlar, J. Phys. Chem. 83, 2921 (1979).
- ⁴³M. Bixon and J. Jortner, J. Chem. Phys. 50, 3284, 4061 (1968); J. Jortner, S. A. Rice, and R. M. Hochstrasser, Adv. Photochem. 7, 149 (1969).
- ⁴⁴P. J. Robinson and K. A. Holbrook, Unimolecular Reactions (Wiley, New York, 1972).
- ⁴⁵T. K. Ha and U. P. Wild, Chem. Phys. 4, 300 (1974).
- ⁴⁶H. F. Shurvell, S. C. Dass, and R. D. Gordon, Can. J. Chem. **52**, 3149 (1974).
- ⁴⁷E. S. Young and C. B. Moore, J. Chem. Phys. **60**, 2139 (1974).
- ⁴⁸S. H. Lin, Proc. R. Soc. (London) Ser. A **352**, 57 (1976).
- ⁴³J. M. F. van Dijk, M. J. H. Kemper, J. H. M. Kerp, and H. M. Buck, J. Chem. Phys. **69**, 2462 (1978).
- ⁵⁰J. Stephenson, J. Chem. Phys. **59**, 1523 (1973).
- ⁵¹P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, J. Chem. Soc. Perkins Trans. 2 14, 1853 (1973).
- ⁵²K. Glänzer, M. Maier, and J. Troe, Chem. Phys. Lett. 61, 175 (1979).
- ⁵³R. D. Levine and J. L. Kinsey, in Atom-Molecule Collision Theory, a Guide for the Experimentalist, edited by R. B. Bernstein (Plenum, New York, 1979).
- ⁵⁴D. J. Bogan and D. W. Setser, J. Chem. Phys. **64**, 586 (1976).
- ⁵⁵K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand, New York, 1979).
- ⁵⁶D. E. Milligan and M. E. Jacox, J. Chem. Phys. 48, 2265 (1968).
- ⁵⁷We are grateful to Professor E. R. Grant for supplying the direct count program.
- ⁵⁸R. G. Bray, R. M. Hochstrasser, and J. E. Wessel, Chem. Phys. Lett. **27**, 167 (1974).
- ⁵⁹ P. H. Turner and A. P. Cox, Chem. Phys. Lett. **39**, 585 (1976).
- ⁶⁰D. H. Levy, B. M. DeKoven, and K. G. Spears (private communication).
- ⁶¹R. D. Bower and P. L. Houston (unpublished data).
- ⁶²S. L. Baughcum and S. R. Leone, J. Chem. Phys. 72, 6531 (1980).