AIP | The Journal of Chemical Physics

State selected ion–molecule reactions by a TESICO technique. VIII. Vibronicstate dependence of the cross sections in the reaction NO+(a 3Σ+,v ; b 3Π,v)+Ar→NO+Ar+

Tatsuhisa Kato, Kenichiro Tanaka, and Inosuke Koyano

Citation: The Journal of Chemical Physics **79**, 5969 (1983); doi: 10.1063/1.445779
View online: http://dx.doi.org/10.1063/1.445779
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/79/12?ver=pdfcov
Published by the AIP Publishing

State selected ion–molecule reactions by a TESICO technique. VIII. Vibronic-state dependence of the cross sections in the reaction $NO^+(a\ ^3\Sigma^+, v; b\ ^3\Pi, v) + Ar \rightarrow NO + Ar^+$

Tatsuhisa Kato, Kenichiro Tanaka, and Inosuke Koyano

Institute for Molecular Science, Myodaiji, Okazaki, 444 Japan

(Received 29 June 1983; accepted 1 September 1983)

Charge transfer reactions $NO^+ + Ar \rightarrow Ar^+ + NO$ (1) have been studied by selecting the vibronic states of NO^+ using the threshold electron–secondary ion coincidence (TESICO) technique. The vibronic states selected were $a\ ^3\Sigma^+$, $v = 0$–5 and $b\ ^3\Pi$, $v = 0$, for each of which the relative cross sections have been determined at two collision energies 1.4 and 5.8 eV. The cross section for the $a\ ^3\Sigma^+$ state has been found to show a resonancelike enhancement at $v = 2$. This feature is reproduced fairly well by the simple two-state theory of Rapp and Francis combined with the consideration of the Franck–Condon factors. However, a closer comparison of the theoretical and experimental results over the entire range of v reveals that the reaction cross sections for the $a\ ^3\Sigma^+$ reactant ion state consist of two components, one in which the vibrational-state dependence is determined simply by the energy defects and Franck–Condon factors, and the other in which the vibrational-state dependence cannot be interpreted by those factors. The cross section for the $b\ ^3\Pi$, $v = 0$ state has been found to be much smaller than those for the exoergic reactions of the $a\ ^3\Sigma^+$ state ($v = 1$–5). This has been attributed to the difference in the nature of the molecular orbitals that play primary roles in the $a\ ^3\Sigma^+$ and $b\ ^3\Pi$ reactions.

I. INTRODUCTION

Although the importance of energy resonance (small energy defect) and favorable Franck–Condon factors in low-energy charge transfer processes involving molecules has been demonstrated in many reaction systems,[1] there still remain controversies concerning their roles. Recent development[2–6] of state selective techniques for studying charge transfer and related ion–molecule reactions has enabled this problem to be examined more critically, allowing direct comparison of the reactions with the same reactant pair in the same electronic states but with varying energy defects and Franck–Condon factors. Experimental results for symmetric charge transfer reactions[2,4(b)] have been compared to calculated cross sections using the multistate impact parameter theory.[7–9]

As to asymmetric charge transfer reactions, Campbell *et al.*[4(a)] studied the reaction $H_2^+(v) + Ar \rightarrow Ar^+ + H_2$ and found that the variation of the cross section as a function of the vibrational quantum number, observed at 20 eV ion translational energy, is in essential agreement with simple calculations based on a model in which cross sections for all possible charge transfer channels are calculated in terms of energy defects (adapting the two-state impact parameter theory of Rapp and Francis[10]) and Franck–Condon factors. Our recent TESICO studies[11,12] have shown that this model agrees well with experiments in some systems but completely disagrees in other systems. Houle *et al.*[5(b)] and Anderson *et al.*,[5(c)] who performed state selected studies of charge transfer reactions in the $H_2^+(v)$, $D_2^+(v) + Ar$ and the $H_2^+(v) + N_2$, CO, O_2 systems, respectively, found that their experimental results are explained quite well in terms of the energy defects and Franck–Condon factors if an exponential gap law is used with a suitable parameter K which takes care of the difference between exoergic and endoergic channels.

In order to further investigate these problems, we have applied, in the present study, our TESICO technique to the vibronic-state selected reactions

$$NO^+(a\ ^3\Sigma^+, v;\ b\ ^3\Pi, v) + Ar \rightarrow Ar^+ + NO\ . \qquad (1)$$

Reaction (1) with NO^+ in the $a\,^3\Sigma^+$ state has been known[13] to have a large cross section and this has been attributed to the close energy resonance between the recombination energy of Ar^+ and a level of NO^+ ($a\,^3\Sigma^+$). As shown in Fig. 1, reaction (1) is endoergic for the ground vibrational state of NO^+ ($a\,^3\Sigma^+$) and is exoergic for $v = 1$ and above.[14–16] In particular, the close energy resonance of the $v = 2$ level with the $Ar^+(^2P_{1/2}) + NO(X\,^2\Pi$, $v = 0)$ product level ($\Delta E \simeq 23$ meV) is to be noted. In

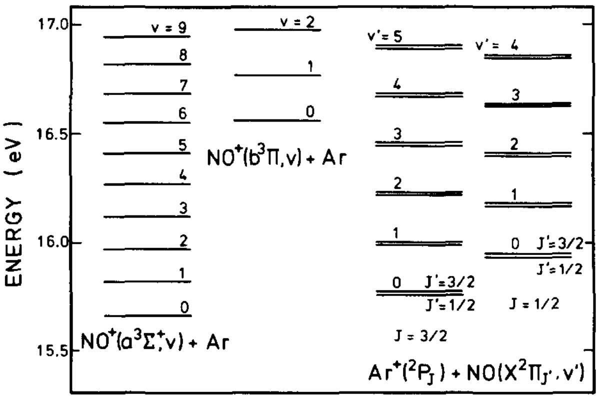

FIG. 1. Energy level diagram for the $(NO + Ar)^+$ system. The spectroscopic data for NO and NO^+ were taken from Refs. 14 and 15 and those for Ar^+ from Ref. 16.

0021-9606/83/245969-06$02.10

addition, the Franck–Condon factor connecting the $NO^+(a\,^3\Sigma^+, v=2)$ and $NO(X\,^2\Pi, v=0)$ states is quite large $(\simeq 0.16)$.[17]

In addition to the above interest, the study of reaction (1) with $NO^+(b\,^3\Pi)$, as compared with that of $NO^+(a\,^3\Sigma^+)$, is expected to provide information on the roles of orbital symmetry and other characteristics of the electronic states in charge transfer reactions. The $NO^+(b\,^3\Pi, v=0) + Ar$ state does not have any resonant product channel, as can be seen from Fig. 1, nor combines with any product state with a favorable Franck–Condon factor (the FC factor ranges 10^{-4}–10^{-6}).[17]

II. EXPERIMENTAL

The threshold electron—secondary ion coincidence (TESICO) technique and the apparatus TEPSICO have been described in detail elsewhere.[3(b)] The essential part of the apparatus consists of a helium Hopfield continuum light source, a 1 m Seya–Namioka monochromator, an ionization chamber, a reaction chamber, a hemispherical electron energy analyzer, and a quadrupole mass spectrometer, these being assembled together via a six-stage differential pumping system. The reactant NO^+ ions are produced in the ionization chamber by the photoionization of NO at the threshold wavelength for each internal state of interest. Reactions take place in a beam-gas mode in the reaction chamber which contains Ar at about 10^{-3} Torr. The mass-analyzed product ions, as well as unreacted primary ions, are then counted in coincidence with the threshold photoelectrons at each wavelength, thus yielding direct information on the state selected reactions. High purity nitric oxide (99.15%) and argon ($\geq 99.999\%$) gases were obtained from Japan Oxygen Co. and used without further purification.

III. EXPERIMENTAL RESULTS

A. Threshold electron spectrum of NO and coincidence spectra of the primary and secondary ions with threshold electrons

The relevant portion of the threshold electron spectrum (TES) of NO, taken with a 0.5 Å bandwidth and about 20 meV electron energy resolution, is shown in Fig. 2. Vibrational intensity distribution in the $a\,^3\Sigma^+$ state is seen to be somewhat different from that observed in the He I spectra.[18] In particular, the $v=1$ peak in the $a\,^3\Sigma^+$ state appears with much higher intensity. This difference is obviously due to the excitation in the TES of the autoionization levels lying very close to an ionic level. Our spectrum is in excellent agreement with that obtained by Stockbauer[19] with a similar resolution.

In the present study, we utilized the vibrational states $v=0$–5 of $a\,^3\Sigma^+$ and $v=0$ of $b\,^3\Pi$ for coincidence experiments. Above the threshold of $v=1$ of the $b\,^3\Pi$ state, assignment of the TES of this resolution is not unique due to overlapping of the levels of the a, b, and $w\,^3\Delta$ states.[19] This restricted the present study to levels up to $v=0$ of $b\,^3\Pi$. Although the $v=0$ state of $b\,^3\Pi$ also overlaps with $v=6$ of $a\,^3\Sigma^+$, the intensity of the former state is far much stronger than that of the latter, allowing the study of the $v=0$ state with sufficient certainty.

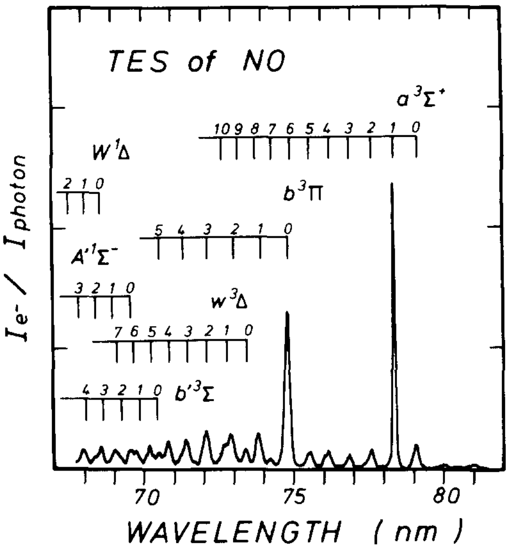

FIG. 2. Threshold electron spectrum of NO obtained with energy resolution of 20 meV (FWHM).

In taking coincidence, the threshold electron signals and the mass-analyzed ion signals are fed, respectively, into the start and stop input of a time-to-pulse height converter. The output signals from this converter are then analyzed by a multichannel pulse height analyzer. The raw data obtained are thus the coinicidence time-of-flight spectra for the primary NO^+ and the secondary Ar^+ ions at each wavelength. Typical examples of our coincidence TOF spectra have previously been shown for other reactions.[11,20–22] From the ratios of the integrated intensities of the TOF peaks for NO^+ and Ar^+, the (relative) cross sections for the individual states were obtained directly.

B. State selected cross sections of reaction (1) for $NO^+(a\,^3\Sigma^+, v=0$–$5)$ and $NO^+(b\,^3\Pi, v=0)$

Relative cross sections of reaction (1) for $v=0$–5 of the $a\,^3\Sigma^+$ state and $v=0$ of the $b\,^3\Pi$ state of NO^+, determined at collision energies of 1.4 and 5.8 eV, are presented in Figs. 3 and 4, respectively. The relative scales in the ordinates are such that the relative cross sections can be compared quantitatively only within a collision energy and not between different collision energies.

As can be seen from the figures, a salient feature in the cross section for the $a\,^3\Sigma^+$ state at these lower collision energies is the sharp resonance-like peak at $v=2$. This enhancement of the $v=2$ cross section is ascribed to the close energy resonance between the $NO^+(a\,^3\Sigma^+, v=2)$ and $Ar^+(^2P_{1/2})$ states, and will be discussed later together with the results of a model calculation. Except the $v=2$ peak, the cross sections tend to increase slowly with increasing vibrational quantum number from $v=0$ to $v=5$. Another point to be noted is the occurrence of the $v=0$ cross section of substantial

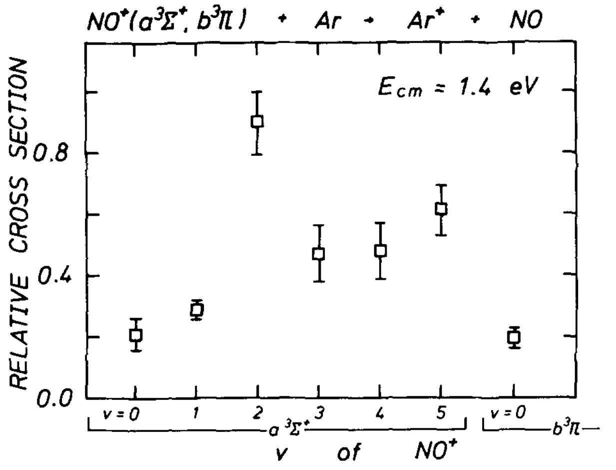

FIG. 3. State selected relative cross section for reaction (1) as a function of vibrational quantum number v of NO$^+$ ($a\,^3\Sigma^+$) and NO$^+$ ($b\,^3\Pi$), obtained at the collision energy of 1.4 eV.

magnitude even at the collision energy of 1.4 eV. Reaction (1) for $v=0$ is endoergic by 0.1 eV and thus the above collision energy exceeds the endoergicity only by 1.3 eV. In this context, reaction (1) seems to be an exceptional case of endoergic charge transfer reactions, since our previous studies[12,20] have indicated that a collision energy that exceeds the endoergicity by a considerable amount (e.g., ~ 10 eV) is usually required in promoting endoergic reaction considerably.

The above features seem to be almost the same for the two collision energies. The only difference to be seen is the somewhat more enhanced $v=3$ cross section at 5.8 eV than at 1.4 eV.

The $v=0$ state of $b\,^3\Pi$, on the other hand, exhibits a very small cross section at these collision energies; the cross section sharply decreases by a factor of ~ 3 in going from $v=5$ of $a\,^3\Sigma^+$ to $v=0$ of $b\,^3\Pi$, and the values at the latter state are even smaller than those for the $v=0$ of the $a\,^3\Sigma^+$ state. This fact is very interesting considering that reaction (1) is endoergic for the $a\,^3\Sigma^+$, $v=0$ state, whereas the energy content of the $b\,^3\Pi$, $v=0$ state far exceeds the endoergicity. This clearly demonstrates that the reaction is governed by (a) factor(s) other than the available energy. One of the factors must be the orbital symmetry as manifested by the $^3\Sigma^+$ and $^3\Pi$ terms, and will also be discussed below.

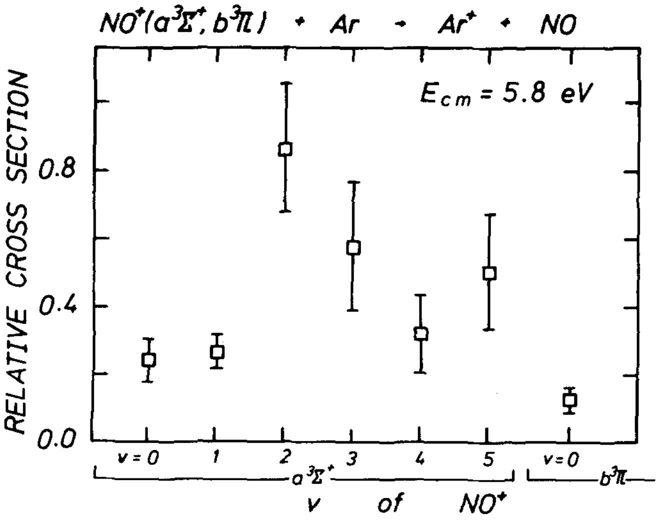

FIG. 4. State selected relative cross section for reaction (1) as a function of vibrational quantum number v of NO$^+$ ($a\,^3\Sigma^+$) and NO$^+$ ($b\,^3\Pi$), obtained at the collision energy of 5.8 eV.

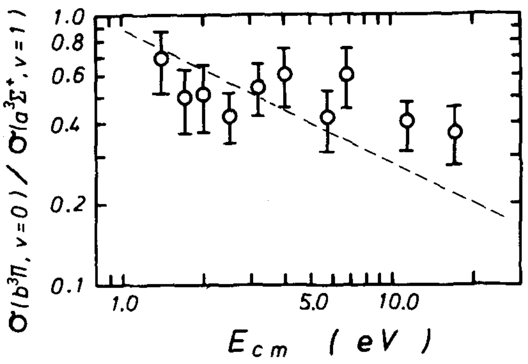

FIG. 5. The ratio of the cross sections for the $b\,^3\Pi$, $v=0$ and the $a\,^3\Sigma^+$, $v=1$ states as a function of collision energy. The broken line indicates the $E^{-1/2}$ dependence.

C. Collision energy dependence

In order to obtain further information on the dynamics of the reactions of the two electronic states, we have also studied the collision energy dependence of the ratio of the cross sections for the $b\,^3\Pi$, $v=0$ and the $a\,^3\Sigma^+$, $v=1$ states: $\sigma(b,0)/\sigma(a,1)$. Ideally, the collision energy dependence of the individual cross sections themselves would be desirable for this purpose. However, with our apparatus the quantitative comparison of the cross sections between different collision energies cannot be made as accurately as the comparison of the cross sections between different processes at a fixed collision energy, because the changing of the collision energy is accomplished by changing the voltages on various electrodes, which in turn somewhat affects the ion collecting efficiency of the apparatus. For this reason, we preferred the ratio of the cross sections. The $v=1$ state was chosen for $a\,^3\Sigma^+$ because this is the first state for which reaction (1) becomes exoergic and, in addition, the intensity of the threshold electrons is strongest for this state.

The results are shown in Fig. 5. Although the ratio seems to have some structure at certain collision energies, it generally decreases with increasing collision energy with a gradient whose absolute value is smaller than 1/2.

IV. MODEL CALCULATION

As in the previous studies,[11,12] we have performed a model calculation of the relative cross sections of reaction (1), assuming that each product channel can be treated independently as a two-state problem to which the impact parameter theory of Rapp and Francis[10] can be applied. The applicability of this theory is briefly discussed in the next section. For reasons described there, the comparison of the calculated and experimental results is expected to give information on the reaction mechanism.

The procedure for the calculation is as follows. The Rapp and Francis cross sections are calculated for each specific pair of the reactant and product states of $\mathrm{NO}^+(a\,^3\Sigma^+, v) + \mathrm{Ar} \rightarrow \mathrm{NO}(X\,^2\Pi, v', J') + \mathrm{Ar}^+(^2P_J)$, according to the equation[10]

$$\sigma(v, v', J', J) = F/2 \int_0^{b'} \mathrm{sech}^2\left[\frac{\Delta E}{h\mathrm{v}}\left(\frac{a\pi b}{2\gamma}\right)^{1/2}\right] 2\pi b\, db \ , \qquad (2)$$

where ΔE is the energy defect between the two states $[(v)$ and $(v', J', J)]$, v the velocity of the NO^+ ions, b the impact parameter, F the statistical weight of the product states, a the radius of the first Bohr orbit of the hydrogen atom, and γ the square root of average ionization energies (in the Rydberg unit) of the two states. b' approximately represents the effective range of impact parameter of the symmetrical resonance charge transfer at velocity v, and is determined according to the tables prepared by Lee and Hasted[23] in a form suitable for practical use. The total charge transfer cross sections for each vibrational state $\sigma(v)$ are then obtained by summing the contribution from each product channel $\sigma(v, v', J', J)\, q_{vv'}$ over $v' = 0 - v'_{\max}$, $J' = 1/2$ and $3/2$, and $J = 3/2$ and $1/2$:

$$\begin{aligned}\sigma(v) = \sum_{v'=0}^{v'_{\max}} [&\sigma(v, v', 1/2, 3/2) + \sigma(v, v', 3/2, 3/2) \\ &+ \sigma(v, v', 1/2, 1/2) + \sigma(v, v', 3/2, 1/2)]\, q_{vv'} \ , \end{aligned} \qquad (3)$$

where $v'_{\max}$ is the maximum value of v' attainable for each collision energy. $q_{vv'}$ are the Franck–Condon factors for the ionizing transitions $\mathrm{NO}(X\,^2\Pi, v') \rightarrow \mathrm{NO}^+(a\,^3\Sigma^+, v) + e$ and are calculated numerically according to the method given by Nicholls.[17]

As an example, we show in Table I absolute values of relevant quantities involved in the calculation of $\sigma(2)$. This example is for the collision energy of 1.4 eV and thus the energetically attainable product state (column 1) actually extends further up to those with $v' = 7$, but only ten states with the smallest energy defects (column 2) are shown here. It is clearly seen from Table I that the Rapp and Francis cross section (column 3) as a function of ΔE has a very sharp peak around $\Delta E = 0$, and thus the contribution to $\sigma(2)$ essentially comes from only a few channels with small ΔE within ~ 0.05 eV. Statistical weight factor F (column 4) for each product state is given by the multiplicity of the spin-orbit states of both Ar^+ and NO. Using these values, together with the Franck–Condon factors (column 5), we calculate $\sigma(2)$ according to Eq. (3) to be 37.5 Å^2.

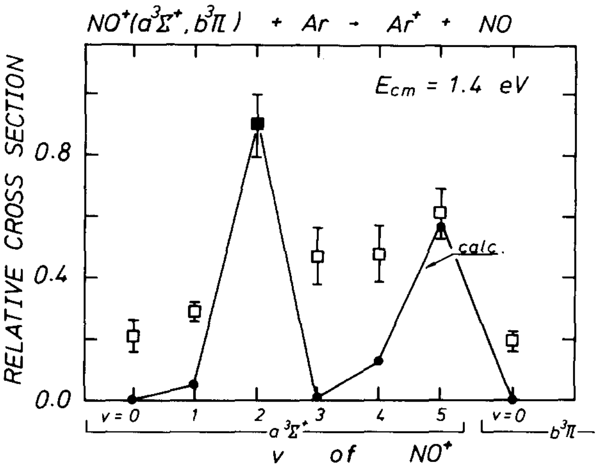

FIG. 6. Calculated cross sections for reaction (1) as compared with the experimental result at 1.4 eV. ●: calculated, □: experimental. The calculated and experimental values are normalized at $v = 2$ of the $a\,^3\Sigma^+$ state.

TABLE I. Numericals for the calculation of $\sigma(2)$. Absolute values of the partial cross sections for the ten product channels (v', J', J) are shown.

$(v'$,	J',	J)	ΔE	$\sigma(v, v', J', J)/F$	F	$q_{vv'}$
(0,	1/2,	3/2)	− 0.216[a] (eV)	0.004 (Å^2)	8	0.172
(0,	3/2,	3/2)	− 0.201	0.005	16	0.172
(0,	1/2,	1/2)	− 0.038	2.906	4	0.172
(0,	3/2,	1/2)	− 0.023	10.740	8	0.172
(1,	1/2,	3/2)	0.017	19.130	8	0.088
(1,	3/2,	3/2)	0.031	5.151	16	0.088
(1,	1/2,	1/2)	0.195	0.005	4	0.088
(1,	3/2,	1/2)	0.209	0.004	8	0.088
(2,	1/2,	3/2)	0.246	0.002	8	0.007
(2,	3/2,	3/2)	0.261	0.002	16	0.007

[a] The negative value indicates that the channel is exoergic.

Absolute values of $\sigma(i)$s obtained in the similar way are: $\sigma(0) = 0.1$, $\sigma(1) = 3.3$, $\sigma(2) = 37.5$, $\sigma(3) = 0.3$, $\sigma(4) = 5.9$, $\sigma(5) = 21.1$, $\sigma(b, 0) = \sim 0.0$, all in the unit of Å^2. In Fig. 6, relative values are compared with the experimental ones. The calculated and experimental values are normalized at $v = 2$.

V. DISCUSSION

From Fig. 6, one may see that the model calculation reproduces qualitatively the two features of the experimental results for the $a\,^3\Sigma^+$ state, i.e., the resonant enhancement of the cross section at $v = 2$ and the increase in the cross section with increasing vibrational quantum number between $v = 0$ and 1 and $v = 3$ and 5. However, the calculated and experimental results are found to be in disagreement with each other when the relative cross sections are compared quantitatively. In particular, it is noteworthy that the experiment gives cross sections of substantial magnitude at $v = 0$ and 3 where the calculation predicts the cross sections of essentially zero when both results are normalized at $v = 2$.

As is well known, the Rapp and Francis theory is a two-state impact parameter theory based on the assumption that the charge transfer is due to potential energy curves lying close together at large internuclear separation (Stueckelberg–Demkov type interaction) rather than localized curve crossings at comparatively small internuclear distances (Landau–Zener type interaction). Also, the Franck–Condon factors are quantities characterizing the reactant and product molecules at infinite separation. Consequently, the model as used here is considered to be applicable only to the systems in which charge transfer takes place by a simple electron jump mechanism (a direct mechanism) at large internuclear separation. Thus, it is hoped that the comparison of the calculated results with experimental ones gives information on the nature of the interaction or the mechanism of the charge transfer. In fact, our previous studies[11,12,24] have shown that the model explains experimental results very well in some systems but does not at all in other systems, presumably reflecting the reaction mechanism in each case. Moreover, the extent to which the model explain the features of experimental results has been found to depend on the collision energy,[12,24] suggesting the occurrence of a change in the reaction mechanism according to the collision energy.

In the present case, the agreement between the experimental and calculated results (in the context of the occurrence of the resonant enhancement at $v=2$) would probably indicate that reaction (1) proceeds, at least to a considerable extent, by an electron jump mechanism at large internuclear separation. At the same time, however, the fact that the relative cross sections involving other vibrational states are considerably larger than those predicted from the model would indicate also that a mechanism other than the simple electron jump is occurring at this energy. This second mechanism must be an electron transfer through some intimate interaction between the reactants, presumably via a collision complex. In such an interaction, the transfer probability would be determined by factors other than those characterizing the reactants and products at infinite separation.

The low charge-transfer probability of the $b\,^3\Pi$ state (although only $v=0$ was studied) as compared with the $a\,^3\Sigma^+$ state is interpreted by considering the difference in the molecular orbitals of NO^+ involved. The electronic configurations of $NO^+(a\,^3\Sigma^+)$, $NO^+(b\,^3\Pi)$, and $NO(X\,^2\Pi)$ are $\cdots(1\pi)^1(5\sigma)^2(2\pi)^1$, $\cdots(1\pi^2)(5\sigma)^1(2\pi)^1$, and $\cdots(1\pi)^2(5\sigma)^2(2\pi)^1$, respectively. Thus, in the reactions with $NO^+(a\,^3\Sigma^+)$ an electron will be transferred from Ar into the 1π vacancy which extends to directions perpendicular to the internuclear axis, whereas in the reaction with $NO^+(b\,^3\Pi)$ the transfer will be into the 5σ vacancy which extends to the direction along the internuclear axis and has more density on the N atom end. Thus, in the former reaction, the broadside collisions covering a wide angle of approach will be effective in causing the charge transfer, while in the latter reaction, only the end-on collisions within a rather small solid angle around the internuclear axis will be effective. This difference in the available angle of approach would probably explain the difference in the magnitude of the cross sections.

In order to obtain some evidence in support of this view, we have also performed an *ab initio* calculation of partial potential energy surfaces of the triplet states of the $(NO\text{–}Ar)^+$ system.[24] The results indicated that two mechanisms are indeed possible for the $NO^+(a\,^3\Sigma^+)+Ar$ interaction, one corresponding to the broadside approach of Ar and the other to the collinear approach. In the broadside approach, the interaction of the 1π orbital of NO and the $3p_x$ orbital of Ar makes the asymptotic $NO^+(a\,^3\Sigma^+)+Ar$ potential stabilize gradually as the internuclear distance is decreased and correlate to the triplet ground state potential of the complex. In this case, a Stueckelberg–Demkov type transition is expected between this state and the excited state of the same symmetry which correlates to the asymptotic $Ar^+(^2P_J)+NO$ state. In the case of the collinear approach, on the other hand, the interaction between the 5σ orbital of NO and the $3p_z$ orbital of Ar makes the asymptotic $Ar^+(^2P_J)+NO$ state correlate to the triplet ground state of the complex, the $NO^+(a\,^3\Sigma^+)+Ar$ asymptotic potential correlating to a repulsive excited state of the complex. Thus, there must be some avoided crossing between these surfaces in order for a charge transfer to occur. This interaction seems to give rise to a Landau–Zener-type transition. These seems to correspond to the two components of the experimental cross section.

Concerning the $b\,^3\Pi$ state reaction, the present *ab initio* calculation cannot give any conclusive information because the $NO^+(b\,^3\Pi)+Ar$ interaction in both nuclear configuration corresponds to excited triplet states. But the fact that the relative cross section at $NO^+(b\,^3\Pi, v=0)+Ar$ state is considerably larger than that predicted from the model calculation would indicate that the reaction of $NO^+(b\,^3\Pi)$ does not proceed by a simple electron jump but by an intimate collision mechanism. The collision energy dependence of the ratio $\sigma(b,0)/\sigma(a,1)$, shown in Fig. 5, also seems to support this interpretation; if the reaction of $NO^+(b\,^3\Pi)$ proceeds by an intimate collision mechanism, its cross section would decrease with increasing collision energy due to the centrifugal barrier to the formation of a complex (Langevin-type behavior). On the other hand, the cross section for the $NO^+(a\,^3\Sigma^+)$ reaction would decrease much slowly, if it does at all, since at least a considerable fraction of the reaction proceeds by a direct mechanism. As a net result of these two modes of variation, the ratio $\sigma(b,0)/\sigma(a,1)$ would decrease less steeply than expected from the Langevin model (the $E^{-1/2}$ dependence) with increasing collision energy. This is in agreement with the experimental results, as shown in Fig. 5.

In conclusion, we have shown experimentally that the cross section of reaction (1) for $NO^+(a\,^3\Sigma^+)$ exhibits interesting dependence on the vibrational state, and that the cross section is reduced considerably when NO^+ is excited to the energetically higher $b\,^3\Pi$, $v=0$ state. Comparison of these cross sections with the calculated ones based on the two-state impact parameter theory and the Franck–Condon factors indicates that the reaction of the $a\,^3\Sigma^+$ state at low collision energies proceeds predominantly by a long-range electron jump mechanism, but a considerable fraction of the reactions also proceeds by an intimate collision mechanism. Consideration of the molecular orbitals and other evidences rationalize the small cross section of the $b\,^3\Pi$ state as compared with those of the $a\,^3\Sigma$ state, and indicate that the reaction with the $b\,^3\Pi$ state may proceed by an intimate collision mechanism.

[1] See, for example, (a) J. B. Laudenslager, W. T. Huntress, Jr., and M. T. Bowers, J. Chem. Phys. **61**, 4600 (1974), and references cited therein; (b) J. Durup, in *Interaction Between Ions and Molecules*, edited by P. Ausloos (Plenum, New York, 1975), p. 619 and references cited therein.

[2] (a) L. Squires and T. Baer, J. Chem. Phys. **65**, 4001 (1976); (b) T. Baer, P. T. Murray, and L. Squires, *ibid.* **68**, 4901 (1978).

[3] (a) K. Tanaka and I. Koyano, J. Chem. Phys. **69**, 3422 (1978); (b) I. Koyano and K. Tanaka, *ibid.* **72**, 4858 (1980).

[4] (a) F. M. Campbell, R. Browning, and C. J. Latimer, J. Phys. B **13**, 4257 (1980); (b) **14**, 3493 (1981).

[5] (a) S. L. Anderson, F. A. Houle, D. Gerlich, and Y. T. Lee, J. Chem. Phys. **75**, 2153 (1981); (b) F. A. Houle, S. L. Anderson, D. Gerlich, T. Turner, and Y. T. Lee, *ibid.* **77**, 748 (1982); (c) S. L. Anderson, T. Turner, B. H. Mahan, and Y. T. Lee, *ibid.* **77**, 1842 (1982).

[6] D. van Pijeren, J. van Eck, and A. Niehaus, Chem. Phys. Lett. **96**, 20 (1983).

[7] D. R. Bates and R. H. G. Reid, Proc. R. Soc. London Ser. A **310**, 1 (1969).

[8] T. F. Moran, M. R. Flannery, and D. L. Albritton, J. Chem. Phys. **62**, 2869 (1975).

[9] T. F. Moran, M. R. Flannery, and P. C. Cosby, J. Chem. Phys. **61**, 1261 (1974).

[10] D. Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962).

[11] T. Kato, K. Tanaka, and I. Koyano, J. Chem. Phys. **77**, 337 (1982).

[12] T. Kato, K. Tanaka, and I. Koyano, J. Chem. Phys. **77**, 834 (1982).

[13] I. Doton, F. C. Fehsenfeld, and D. L. Albritton, J. Chem. Phys. **71**, 3280, 3289 (1979).

[14] D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, J. Chem. Phys. **71**, 3271 (1979).

[15] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules* (Van Nostrand–Reinhold, New York, 1979), Vol. IV.

[16] C. E. Moore, Circ. 467, U. S. Dept. of Commerce (1949) Washington, D.C.

[17] R. W. Nicholls, J. Res. Natl. Bur. Stand. A **65**, 451 (1961).

[18] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules* (Japan Scientific Society, Tokyo, 1981), p. 28.

[19] R. Stockbauer, Adv. Mass Spectrom. **8**, 79 (1980).

[20] K. Tanaka, T. Kato, and I. Koyano, J. Chem. Phys. **75**, 4941 (1981).

[21] K. Tanaka, J. Durup, T. Kato, and I. Koyano, J. Chem. Phys. **74**, 5561 (1981).

[22] K. Tanaka, T. Kato, P.-M. Guyon, and I. Koyano, J. Chem. Phys. **77**, 4441 (1982).

[23] A. R. Lee and J. B. Hasted, Proc. Phys. Soc. London **85**, 673 (1965).

[24] T. Kato (to be published).