ROTATIONAL STATE DEPENDENCE OF TRANSIENT LINEWIDTHS IN THE CO_2 00^01 VIBRATIONAL LEVEL DUE TO TRANSLATIONAL ENERGY RECOIL FROM HOT H AND D ATOM COLLISIONS

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The nascent transient linewidths of the CO_2 00^01, $J \rightarrow 00^02$, $J-1$ transitions were measured immediately following collisions with hot H and D atoms of 2.30 and 2.16 eV energy, respectively. All lineshapes were well fitted by Gaussian profiles, but were significantly broader than the room-temperature Doppler profiles. D atom collisions resulted in broader linewidths than H atom collisions. The observed widths are in good agreement with a simple billiard ball model for a specific rotational level J. However, the linewidth was observed to increase with increasing rotational state within the 00^01 manifold for both hot H and hot D atom collisions.

1. Introduction

Substantial progress has been made recently in measuring the internal state distributions of CO_2 molecules after collisions with hot atoms [1–7]. Initial results of classical trajectory studies have provided encouraging agreement with experiment [8]. Very little, however, is known about the translational recoil of the collision partners in these hot atom experiments, or for that matter in any atom/triatomic molecule collisional encounter. In principle, such information can reveal additional clues about the underlying dynamics. Time-resolved laser "Doppler spectroscopy" is a powerful technique for determining these translational energy distributions [9,10].

In this paper we present a technique for measuring the translational energy distribution of CO_2 molecules resulting from a single collision with a hot H or D atom produced by excimer laser photolysis of H_2S or D_2S. The method is based on time-resolved sub-Doppler infrared diode laser absorption spectroscopy, and has been applied here to obtain initial results on the rotationally resolved collisional excitation of the first excited asymmetric stretch level of CO_2, 00^01. The 0.0003 cm^{-1} resolution of the diode laser is an order of magnitude narrower than the room-temperature Doppler width of the very strong 4.3 μm carbon dioxide spectral transition (fwhm = 0.00424 cm^{-1} at 298 K). Submicrosecond time resolution at low pressures allows a measurement of the CO_2 linewidth to be made following a hot atom/CO_2 encounter but before subsequent collisional relaxation can reestablish a room-temperature Doppler profile.

Prior studies [5–7] have shown that hot H/CO_2 and D/CO_2 collisions establish a non-Boltzmann *rotational* distribution for CO_2 00^01 which peaks at about $J=31$. Although the efficiency of excitation of the 00^01 level by hot H atoms is approximately 2.5 times greater than excitation by hot D, the D atoms become more effective relative to H as the rotational quantum number J increases [6].

The basic experimental approach can be described

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as follows. First, hot hydrogen or deuterium atoms are created by ArF excimer laser photolysis of H_2S or D_2S:

$$H_2S + h\nu(193\,\text{nm}) \rightarrow H^* + HS \quad (E_{\text{trans}} = 2.30\,\text{eV}),$$

$$D_2S + h\nu(193\,\text{nm}) \rightarrow D^* + DS \quad (E_{\text{trans}} = 2.16\,\text{eV}).$$

The hot atoms collisionally excite carbon dioxide:

$$H^* + CO_2(00^00; J'; V') \rightarrow H + CO_2(00^01; J; V).$$

Here V is the velocity of the carbon dioxide molecule, J its rotational angular momentum, and 00^01 is the first excited level of the asymmetric stretch mode. A continuous wave (cw) tunable semiconductor diode laser probes the time-dependent change in the population of a given CO_2 quantum state, for molecules with a specific velocity component along the probe direction, via the P-branch transition of the strong asymmetric stretch band:

$$CO_2(00^01; J; V) + h\nu(4.3\,\mu\text{m}) \rightarrow CO_2(00^02; J-1; V).$$

Since collisional excitation produces very little population in the 00^02 vibrational level, the absorption probe monitors only 00^01 [7].

2. Experimental

25 mTorr of a 1:1 mixture of H_2S and CO_2 or D_2S and CO_2 flows through a 2.7 m (9 foot) sample cell. Excimer and diode beams are made collinear by means of a dichroic beamsplitter which reflects at 193 nm but transmits the infrared laser light. Irises at each end of the sample cell reduce both beams to a 5 mm diameter. A second beamsplitter removes the UV light at the end of the cell, and the infrared beam passes through a monochromator (to separate different diode modes) and is focused onto an InSb detector with ≈ 600 ns response time. Signals are amplified and averaged on a LeCroy 9400 digital oscilloscope. Further details of the apparatus have been described elsewhere [7].

During the experiment the diode is modulated at typically 300 Hz over a frequency range of about 0.01 to 0.015 cm^{-1} (3–4 room-temperature CO_2 linewidths). An auxillary discharge reference cell and a lock-in amplifier with a feedback loop into the diode current control are used to guarantee that each sweep of the modulation cycle samples the same region of spectral frequency space. Different positions within the Doppler profile are then sampled by firing the excimer at different delay times with respect to the start of the modulation cycle. This method works because the transient signals are on a microsecond timescale, while the diode modulation is on a millisecond timescale. This technique allows the entire experiment to be performed while locked onto a spectral line, thereby virtually eliminating any long-term laser drift. The wavenumber axis was calibrated with a Fabry–Perot etalon. Computer control of the diode modulation and the laser firing sequence has been implemented in these experiments.

3. Results

The experiment was performed on three rotational levels of the 00^01 vibrational state ($J = 13$, 35, and 57) using the P(13), P(35), and P(57) transitions of the $00^01 \rightarrow 00^02$ vibrational band. Typical time-resolved absorption signals for $J = 35$ are shown in fig. 1. All signals showed a detector-limited fast rise which is attributed to collisions of hot atoms with CO_2. The detector response of about 600 ns is substantially faster than the background gas collision time (4 μs at 25 mTorr). Thus the fast rise amplitudes are proportional to the nascent population of CO_2 molecules produced in a given rotational level with a specific translational velocity by hot atom collisions. The slow component of the signal which occurs after this initial fast rise represents translational and rotational relaxation.

A plot of the fast rise amplitudes versus detuning from line center gives the nascent Doppler and hence velocity recoil profile for a specific rotational level of the 00^01 vibrational state. In addition, a measurement of amplitudes at later times shows the collapse of the lineshape back to a room-temperature Doppler/velocity profile. The lineshape profiles are shown in fig. 2 for 00^01 P(35). In all cases the data were well fit by Gaussian functions. Fig. 3 shows the fitted nascent linewidths for both H* and D* collisions as a function of rotational quantum number.

The most immediately apparent feature of fig. 3 is that all of the linewidths measured were significantly

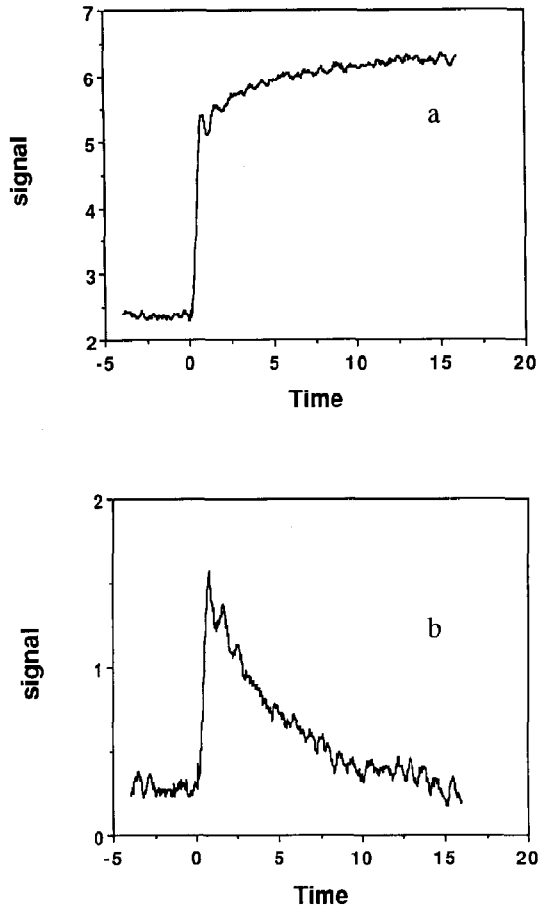

Fig. 1. Typical time-resolved changes in the infrared diode laser probe signal after excimer laser photolysis of H_2S at 193 nm. The x axis is the time in μs after the excimer fires. The y axis is absorption signal in arbitrary units. The probed CO_2 line is 00^01 P(35). Shown in (a) is the signal with the diode laser at line center. Shown in (b) is the signal with the diode laser detuned by 0.005 35 wavenumbers to the high-frequency side of line center.

broader than the room-temperature Doppler width of CO_2 (fwhm = 0.00424 cm^{-1}). The linewidth for H* collisions which produce 00^01 P(35) corresponds to a translational temperature of 1240 K. Deuterium atom collisions give about 20–30% broader linewidths than hydrogen atom collisions for the same rotational state. The estimated error bars for these linewidths are about 10–15%, which arise primarily from inaccuracies in the frequency calibration. While the nascent linewidths observed with the present signal-to-noise ratio conditions appear to be symmetrical about line center, small asymmetries in velocity profile cannot be ruled out at this time.

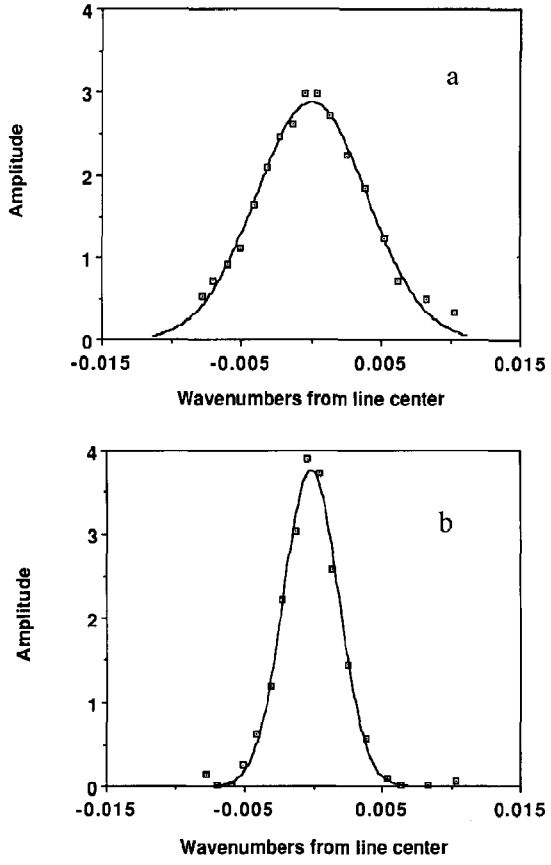

Fig. 2. Lineshape profiles for 00^01 P(35) after collision with hot H atoms at 2.3 eV. The squares are experimental data; the curves are best fits to a Gaussian lineshape. (a) shows the nascent lineshape, 700 ns after the excimer laser fires, before collisional relaxation. (b) shows the lineshape 10 μs after the excimer laser fires, after 2–3 gas kinetic collisions. Signals were taken at 25 mTorr of a 1:1 H_2S/CO_2 mixture.

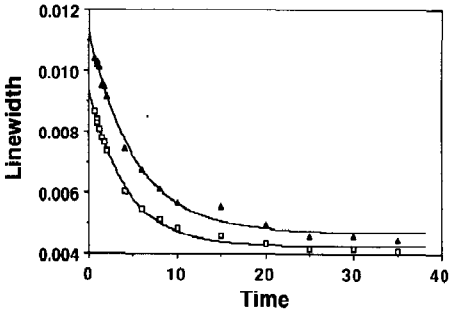

Fig. 3. Fitted linewidth (fwhm) of CO_2 after collision with hot H and D atoms as a function of rotational quantum number J. The open squares are for H atom collisions, and the solid triangles are for D atom collisions. For comparison, the room-temperature Doppler width of CO_2 is 0.004 24 cm^{-1}.

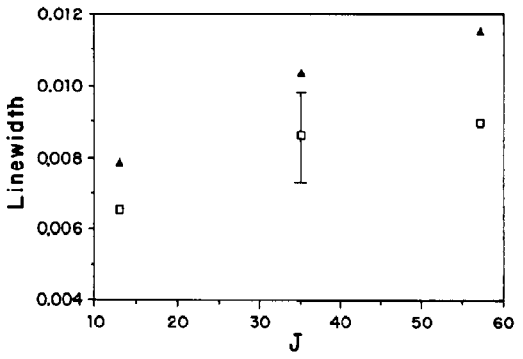

Fig. 4. Fitted linewidth (fwhm) of CO_2 in the 00^01, $J=35$ state after collision with hot atoms as a function of time after the excimer laser pulse. The x axis is time in μs after the excimer fires. The y axis is the full width at half maximum of the lineshape, in cm^{-1}. The open squares are for H* atom collisions, and the solid triangles are for D* atom collisions. The solid curves are the best fit of the data to an exponential decay of the form $y=a+b\exp(-kt)$. For H*, the fit gives $a=0.0042$ cm^{-1}; $b=0.0052$ cm^{-1}, $k=0.24$ μs^{-1}. For D*, the fit gives $a=0.0047$ cm^{-1}, $b=0.0066$ cm^{-1}, $k=0.19$ μs^{-1}. The total pressure is 25 mTorr.

By measuring signal amplitudes at times later than the detector response time, the "translational" relaxation of the linewidth back to the room-temperature Doppler width can be observed. Fig. 4 shows the fitted linewidth for 00^01 P(35) as a function of time after the excimer laser pulse. Given the collision time of about 4 μs at these pressures, the relaxation back to a room-temperature Doppler profile can be seen to be roughly gas kinetic.

Experiments have also been performed in which the 01^10 P(49) and P(59) transitions were monitored. The error bars are larger for these states because the signal quality is poorer, but preliminary results indicate somewhat broader linewidths for the 01^10 bending vibrational level than for the 00^01 asymmetric stretch level.

4. Discussion

Since the vibrational excitation energy (2349 cm^{-1} for 00^01) is relatively small for a typical hot atom/CO_2 encounter compared to the initial collision energy E_0 (approximately 18000 cm^{-1}), the simplest reasonable model for the linewidths observed in the present experiments is a billiard ball, elastic collision model in which H* or D* transfers translational energy to the CO_2 more or less independently of the vibrational excitation. The average energy transferred in such a model is [11]

$$\Delta E=[2M_aM_{CO_2}/(M_a+M_{CO_2})^2](E_0-2349),$$

where M_{CO_2} is the carbon dioxide mass, M_a is the mass of H* or D*, 2349 is the energy in cm^{-1} transferred to vibration, and $E_0=18555$ cm^{-1} (2.30 eV) for H*, $E_0=17426$ cm^{-1} (2.16 eV) for D* are the translational energies of the hot atoms produced by the excimer laser photolysis. The total average translational energy after a hot atom/CO_2 collisional encounter is $E_T=\frac{3}{2}kT+\Delta E=312+\Delta E$ cm^{-1}. Table 1 shows linewidths calculated using this simple model as well as the observed linewidths determined in the present experiments for the P(35), $00^01\rightarrow00^02$ transition of CO_2 immediately following a hot atom/CO_2 collision. The calculated linewidth were assumed to scale as $(E_T/312)^{1/2}$ times the room-temperature Doppler linewidth of 0.0042 cm^{-1}. A comparison of

Table 1
Observed and calculated linewidths of H*/D*+$CO_2(00^00; J'; V')\rightarrow$H/D+$CO_2(00^01; J; V)$ and $CO_2(00^01; J; V)+h\nu(4.3\ \mu m)\rightarrow CO_2(00^02; J-1; V)$

Sample	E_T (cm^{-1}) [a]	$(E_T/312)^{1/2}$	$\Delta\nu_D$ (cm^{-1}) [b]	$\Delta\nu_D$ (cm^{-1}) [c]
CO_2(300 K)	312	1.00	0.0042	
H*/CO_2	1016	1.81	0.0076	0.00865
D*/CO_2	1566	2.24	0.0094	0.0104

[a] $E_T=312+(E_0-2349)[2M_aM_{CO_2}/(M_a+M_{CO_2})^2]$, where $E_0=2349$ cm^{-1} for CO_2(300 K); $E_0=18555$ cm^{-1} for H*; $E_0=17426$ cm^{-1} for D*; $M_{CO_2}=44$ is the mass of CO_2; $M_a=1$ for H* and 2 for D* are the masses of hydrogen and deuterium. The energy of a $CO_2(00^01)$ vibrational quantum is 2349 cm^{-1}.

[b] Linewidth calculated from $\Delta\nu_D=0.0042\ (E_T/312)^{1/2}$.

[c] Linewidth observed experimentally for the P(35) $00^01\rightarrow00^02$ transition. The error limits for these linewidths are ± 15%.

the observed and calculated linewidths clearly indicates that the simple billiard ball model can be used to explain the approximate magnitude of the linewidth increase and its change with collision partner mass.

Although the simple model gives a rough picture of the overall effect, it cannot be used to predict the more subtle changes which are observed in the post-collision linewidths as a function of rotational state, shown in fig. 3. Note that the linewidths increase as final J increases, eliminating an explanation based on energy conservation. If energy limits were important, the linewidth would decrease (decreasing translational energy) as J increases (increasing rotational energy). There are at least two possible origins for this effect. First, there may be vector correlations in the collision process which affect higher rotational levels more than lower J states [9]. Since the diode laser probes velocity components only along its propagation direction, changes in linewidth can also occur if the CO_2 recoil direction changes with rotational state. This appears to be unlikely since the excimer laser used was randomly polarized in these experiments and would be expected to smear out any directional memory of the photodissociation and collision events. Nevertheless, directional changes cannot be ruled out at the present time and must be checked in future work using a laser with a unique polarization. Second, the change in linewidth with rotational state must also reflect the way in which the differential cross section changes with J and impact parameter [12–14]. The rigid ellipsoid model provides a simple picture which can be used to predict the CO_2 recoil velocity and angular momentum as a function of H/CO_2 impact parameter and angle of approach with respect to the CO_2 axis [15,16]. Using the ellipse parameters $A=2$ Å (semi-major axis) and $B=1$ Å (semi-minor axis), this model predicts increasing CO_2 recoil with increasing CO_2 angular momentum in the scattered product for impact parameters greater than about 0.7 Å. At impact parameters smaller than about 0.7 Å, the CO_2 recoil is found to be roughly independent of product CO_2 angular momentum.

5. Conclusions

The linewidths of several rotational states of the 00^01 vibrational state of CO_2 have been measured after collisions with hot H* and D* atoms in the absence of collisional relaxation. All Doppler profiles could be well fit by a Gaussian function. The resulting linewidths were 1.5–3 times larger than room-temperature CO_2 linewidths, but collapsed back to a room-temperature Doppler profile on a gas kinetic timescale. In addition, the observed linewidths increased with increasing rotational quantum number. A simple billiard ball model can account for the dependence of linewidth on hot atom mass, but not the dependence on CO_2 rotational quantum number. However, calculations using a rigid ellipsoid model do predict increasing CO_2 recoil velocity with increasing product CO_2 angular momentum, at least for some range of impact parameters.

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