Collision Relaxation Cross Section of Highly Vibrationally Excited Molecules

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Through quantum-beat spectroscopy collision relaxation of a high vibrational level of SO_2 at 44 877.52 cm^{-1} is characterized. This is a first measurement of collision relaxation for a single, highly excited vibrational level. The deduced relaxation cross section of this excited level by Ar is 216 $\mathrm{Å}^2$, 5 times the area of the hard sphere, and by an ambient temperature SO_2 molecule is 969 $\mathrm{Å}^2$, almost 20 times the hard sphere. These cross sections indicate that relaxation collisions of highly vibrationally excited molecules have effective distances much longer than van der Waals radii and involve mechanisms qualitatively different from lower excitations.

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In order to understand how molecular excitation influences reactivity, it is imperative that we characterize energy transfer of excited molecules. Toward this goal, collision energy transfer of molecules excited with high vibrational energies has been studied for decades. But, due to experimental difficulties, so far in most studies only ensembles of molecules with wide energy distributions, rather than a well-defined energy, have been examined.

In order to quantify the amount of energy removed per collision, it is first necessary to determine which cross section to use for defining a collisional encounter: whether it should be a hard sphere, as defined by repulsive forces; the Lennard-Jones (L-J) cross section, as intermolecular potential should be taken into account in the approach of the colliders [1]; or an even larger cross section as recent studies have suggested that long range interactions contribute to energy transfer of highly excited molecules [2,3]. Here, we report for the first time the measurement, by the application of quantum-beat spectroscopy, of the collision cross section of a single, highly excited vibrational level with a well-defined energy.

The relaxation collision cross section of a single quantum state can be deduced directly from its population decay rate if the relative velocity of the colliding molecules is known. Because of difficulties in preparing and probing molecules with well-defined energy, state specific studies of highly vibrationally excited molecules so far have had limited success. Single-photon overtone excitation has been used to reach H-stretching overtone levels [4]. Multiple resonance techniques such as stimulated emission pumping may excite Franck-Condon allowed molecular eigenlevels [5]. These techniques have enabled measurements of collision energy transfer of a single level in modest energy or level density regions.

The primary difficulty in preparing a high vibrational level directly from a thermal population stems from the fact that the optical transition between the two is forbidden. In some circumstances, however, the optically "dark," high vibrational state may be detected through coupling with an optically "bright" level, usually an excited electronic state accessible through an allowed transition. The coupling between the two zeroth order bright and dark states creates a pair of eigenlevels with each containing a piece of the bright state wave function, through which the entire eigenlevel, including the dark state wave function, can be excited. A coherent excitation of the two eigenlevels induces quantum interference which results in an oscillation of the zeroth-order wave functions in time. A well-known quantum interference phenomenon is the fluorescence quantum beat which is induced through the excitation of the bright state, but its decay depends also upon the dark state properties and can be used for the characterization of the dark state.

Most quantum beats observed for molecules originate from the coupling between an excited singlet state and a triplet state and have been used for studying the triplet or nonzero spin states [6–9]. But a few cases related to transitions in the SO_2 $\tilde{C} \leftarrow \tilde{X}$ bands have been determined to involve highly vibrationally excited levels of the electronic ground state. From the lack of response in quantum-beat frequency to an applied magnetic field, Wallace and co-workers [10] concluded that the dark levels are the $\tilde{X}$ state high vibrational levels.

The SO_2 ${}^{q}R(6)_{1,5}$ $1_0^2 2_0^1 3_0^0$ $\tilde{C} \leftarrow \tilde{X}$ transition at 44 861.39 cm^{-1}, exhibiting strong quantum beat in fluorescence, provides an opportunity for us to access a single vibrational state with 44 877.52 cm^{-1} energy above the zero point. The magnitude of the fluorescence intensity modulation indicates that the two zeroth-order states, a $\tilde{C}$ (210) $7_{1,6}$ rovibronic state and an isoenergetic $\tilde{X}$ high vibrational state, are strongly coupled, creating two eigenlevels whose properties are equally influenced by both zero-order states. The quantum-beat frequency, intensity modulation depth, and decay rate are determined by the coupling matrix element, energy difference, and lifetimes of the zeroth-order states. Of these molecular parameters, only the lifetimes are pressure dependent. By monitoring the quantum-beat decay as a function of pressure, we can measure the collisional relaxation lifetimes of both the bright as well as dark states.

Experiments with samples prepared in either a supersonic expansion or a gas cell were performed. In order

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to determine the *collisionless* eigenlevel properties, fluorescence from a supersonic jet formed by 0.5% SO_2 seeded in an expansion of 15 psi Ar through a 350 micron nozzle was recorded 2.5 cm downstream. Pressure dependent studies were carried out in a room temperature gas cell where the pressure was monitored by a capacitance manometer (MKS, 0–1 Torr). The cell was initially filled with 5 mTorr SO_2, and then the collider gas, He, Ar, or ambient SO_2, ranging from a few mTorr up to 1 Torr, was added.

The excitation source was an Excimer pumped dye laser (Lambda Physik EMG 201/FL 2002), with its output frequency doubled by a beta barium borate crystal. The laser pulse width was 10 ns and the bandwidth 0.06 cm^{-1}. Fluorescence was detected perpendicularly to the laser beam path by a photomultiplier tube with a 2 ns rise time, processed by a 400 MHz transient digitizer, and averaged 256 times.

The fluorescence quantum beat measured in the supersonic jet is shown in Fig. 1. The fluorescence decay can be analyzed according to a coupled two level system, where the two eigenstates $|1\rangle$ and $|2\rangle$ are linear combinations of the zero-order wave functions $|b\rangle$ (bright) and $|d\rangle$ (dark), e.g., $|1\rangle = C_{1b}|b\rangle + C_{1d}|d\rangle$. As the dye laser output consists of several longitudinal modes within the 0.06 cm^{-1} width, the fluorescence intensity in time should be best analyzed by the model developed by Jiang and Brumer [11] for a partially coherent light source:

$$\begin{aligned} I(t) \sim\ & C_{1b}^4 \exp(-\gamma_1 t) + C_{2b}^4 \exp(-\gamma_2 t) \\ & + 2\xi\, \mathrm{Re}\{|C_{1b}|^2 |C_{2b}|^2 \exp[-(\gamma_1 + \gamma_2)t/2] \\ & \times \exp[-i(\omega_{12} t + \theta)]\}, \end{aligned} \tag{1}$$

where θ is the phase difference of the fluorescence from the two eigenstates at $t = 0$, ω_{12} is the angular frequency corresponding to the energy difference of the two eigenstates, and γ_1 and γ_2 are the eigenstate decay constants. ξ is a parameter depicting the effect of the phase correlation of the optical fields experienced by the two eigenlevels.

A nonlinear least squares fit of Fig. 1 to Eq. (1) gives $\xi = 0.75 \pm 0.03$ and a system response time of 12.5 ± 0.1 ns; both are reasonable values. Most significantly, the fit gives $(C_{1b})^2 = (C_{2b})^2 = 0.50$, indicating an equal mixing of two isoenergetic, zeroth-order states. Under collisionless conditions, the $\tilde{X}$ state radiative decay rate is orders of magnitude slower than that of the $\tilde{C}$ state. Therefore, the decay constant of the eigenlevel, which consists of 50% of the $\tilde{C}$ state, is expected to be half of that of the $\tilde{C}$ state. From the fitting we have determined a collisionless lifetime of 31.97 ns for the $\tilde{C}$ (210) $7_{1,6}$ state. From the beating frequency, the energy difference between the two eigenlevels is determined to be $6.96 \pm 0.04 \times 10^{-4}\ \text{cm}^{-1}$, which gives a $3.5 \times 10^{-4}\ \text{cm}^{-1}$ coupling matrix element between the $\tilde{X}$ and $\tilde{C}$ zeroth-order states.

Information on collisional relaxation is contained in the pressure dependent cell experiments. A few fluorescence traces collected with different Ar pressures are shown in Fig. 2. At room temperature, SO_2 rotational transitions are congested even at 0.06 cm^{-1} resolution. Therefore, the fluorescence detected from the gas cell has two contributions, one from the transition which shows the beating pattern and the other from background transitions that are in near resonance with the laser frequency. Analysis of the cell fluorescence decays has been performed using a sum of the two parts:

$$\begin{aligned} I(t) \sim\ & [1/2 + \xi \cos(\omega_{12} t + \theta)] \exp(-\gamma t) \\ & + B \exp(-\gamma_{nb} t). \end{aligned} \tag{2}$$

The first term represents Eq. (1) under the conditions that all mixing coefficients squared are 0.50 and $\gamma = \gamma_1 = \gamma_2$. B represents the portion of the fluorescence from the nonbeating background transition. γ_{nb} is the average decay constant of the excited background states.

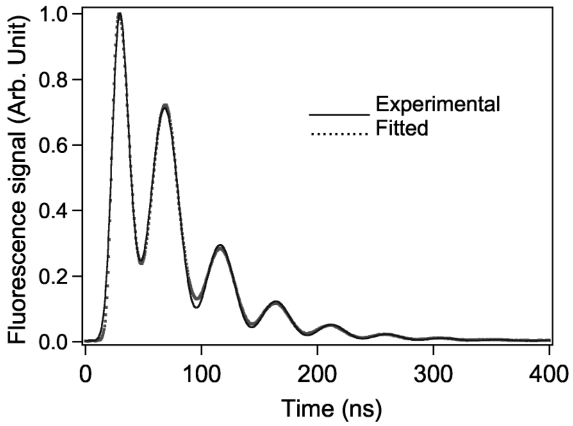

FIG. 1. Fluorescence decay following excitation of the $^{q}R(6)_{1,5}$ $1_0^2 2_0^1 3_0^0$ $\tilde{C} \leftarrow \tilde{X}$ transition of SO_2 in a supersonic jet under collisionless conditions.

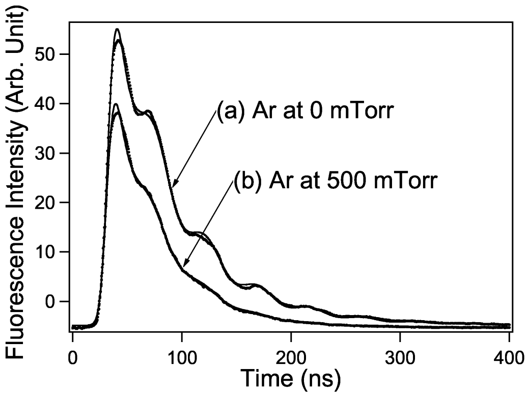

FIG. 2. Fluorescence decays following excitation of the designated transition of 5 mTorr SO_2 in a static cell with Ar pressures as shown. The dotted curve is experimental. The solid curve is the fit.

The parameters directly extracted from the fluorescence decays are for the molecular eigenlevels, which can be related to the zeroth-order state properties through a perturbation treatment [12]. In particular, $\gamma_1 = C_{1b}^2\gamma_b + C_{1d}^2\gamma_d$, $\gamma_2 = C_{2b}^2\gamma_b + C_{2d}^2\gamma_d$, and $\gamma_1 + \gamma_2 = \gamma_b + \gamma_d$. Both γ_b and γ_d consist of a unimolecular decay contribution and a collisional decay component that is linearly proportional to pressure. Once the decay constants of the eigenlevels as well as the bright state are known, the relaxation rate constant of the dark state can be determined.

In Fig. 3, γ_{nb} and γ are plotted against the Ar pressure. In these Stern-Volmer plots, the slope is the collision decay constant. From γ, the eigenlevel decay constant is determined as 21.2×10^6 $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$. From γ_{nb}, the average decay constant of the background $\tilde{C}$ state levels is determined as 7.47×10^6 $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$. This mean value is used as the $\tilde{C}$ (210) $7_{1,6}$ state collision rate constant.

It is imperative that the observed quantum-beat decay originates from depopulation, rather than dephasing of the coherent excitation, of the eigenstates, so that Eq. (2) can be used. If depopulation and dephasing both contribute significantly to the quantum-beat decay, the beat amplitude and the overall intensity would decay with different rates as was shown by density matrix treatment of the quantum-beat decay [13,14]. Collision may also induce mixing of the two eigenlevels since between them there is nonzero transition dipole arising from the two different zeroth-order states [15]. This mixing may contribute to the dephasing and cause a change in the beat frequency, a point also alluded to in Ref. [14]. These concerns can be best examined in *collision* induced quantum-beat decay observed in a supersonic jet where the beat exhibits nearly full amplitude modulation as shown in Fig. 1. In the supersonic jet, the fluorescence from molecules experiencing collisions can be detected at distances closer to the nozzle and at higher stagnation pressures. Figure 4 shows that each fluorescence decay trace taken at collisional conditions can be described by a *single* decay constant governing both beat amplitude and overall intensity decays (even though the exact collision frequency in the jet is unknown). This observation indicates that dephasing makes negligible contribution to the quantum-beat decay, since its amplitude decays at the same rate as the overall intensity which is a depopulation event. Furthermore, there is no detectable change (<1%) in the beat frequency.

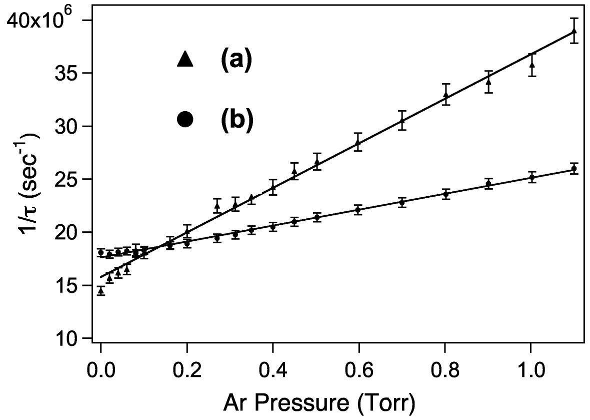

FIG. 3. The decay rate of (a) the eigenlevels extracted from fluorescence quantum beat and (b) the background, nonbeating fluorescence, as a function of the Ar pressure.

With all the other rate constants pinned down, the collision relaxation rate of the dark, high vibrational state can now be determined. For the Ar collider, this rate constant is 3.5×10^7 $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$ which corresponds to a 216 Å^2 cross section, 5 times the hard sphere cross section of 44 Å^2. The cross section by the ambient SO_2 is 969 Å^2, almost 20 times larger.

What is the reason for this large cross section? First, it should not be the result of large amplitude motion of a highly vibrationally excited molecule alone. Estimates by the breathing sphere model [16] or the Morse potential with the entire 44 877.52 cm^{-1} in the S-O bond give a cross section smaller than 85 Å^2 for SO_2-Ar. It is most telling by comparing the cross sections by the three different colliders (Table I). If the SO_2 vibrational amplitude were a dominating factor, the three cross sections should have comparable magnitudes.

The $\tilde{X}$ high vibrational state has a much larger collision decay constant in comparison with the isoenergetic $\tilde{C}$ (210) $7_{1,6}$ state. Both the $\tilde{X}$ and $\tilde{C}$ states have the same total angular momentum. The $\tilde{C}$ state collision rate constant by Ar is about gas kinetic, which is what is expected of rotational relaxation of a polar molecule by an inert gas atom. For the $\tilde{X}$ high vibrational level, there are at least two qualitative differences for rotational relaxation: the K rotational quantum number is not expected to be good because of rotation-vibration coupling [17], and the vibrational level

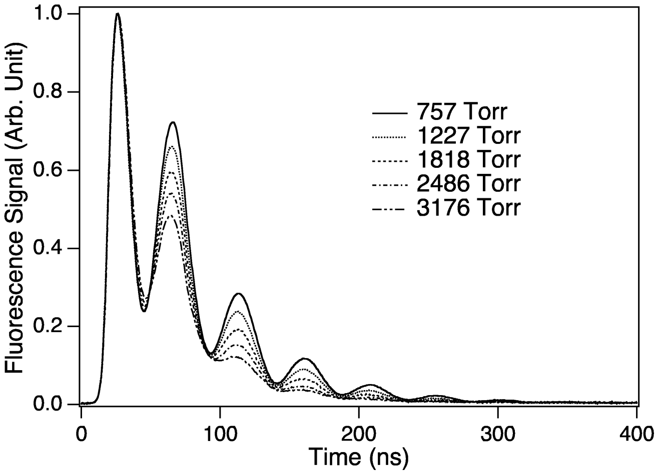

FIG. 4. Fluorescence decays following the excitation of the designated transition of SO_2 (0.5%) seeded in an Ar supersonic expansion, with different stagnation pressures shown. The fluorescence was monitored at 3 mm from the nozzle. The intensities are normalized at the maximum.

TABLE I. Collision cross sections (in Å^2) of highly vibrationally excited SO_2^* with different colliders at 297 K.

Colliding pair	Hard sphere	L-J	Experimental
SO_2^*/He	35	34	87
SO_2^*/Ar	44	60	216
SO_2^*/SO_2	53	87	969

density is much higher. The relaxation of the K selection rule and the smaller energy gap afforded by the high level density should both enhance the rotational relaxation rate, though it is far from clear how much an increase is due to pure rotational relaxation. This same question was raised by studies of collisional quenching of excited rovibronic levels in the $\tilde{A}^1A_2$ state of SO_2 by Ar [18,19], where cross sections twice the size of the hard sphere were reported and attributed to vibronic relaxation caused by dipole-induced dipole and dispersion interactions.

For vibrational relaxation, it has long been recognized that a hard sphere does not properly reflect the range of interactions for molecules excited with abundant energy. Models have been developed to take into account the full Lennard-Jones potential, not just the repulsive wall. Such L-J cross sections are (20–50)% larger than the hard sphere for most molecules at room temperature [1].

Recent experimental measurements on the energy removal rate [3] and quantum state distribution following quenching [2] of highly vibrationally excited molecules have suggested the involvement of the downward transition dipole of the excited molecule in the quenching mechanism. In vibration-translation energy transfer, there is evidence suggesting a mechanism depicted by dispersion force involving the transition dipole [3,20]. Even in collision energy transfer of highly excited diatomics where the vibrational level density is much lower, studies have substantiated the importance of long range interactions involving a transition dipole [15]. This long range interaction, in contrast to the short range interaction defined by the repulsive wall, implies a larger collision cross section. The possible contribution of this long range interaction to the cross section is indicated in the relative ratio of the measured cross section to the hard sphere for the three colliders. In the case of quenching by He, the long range interaction is minimal due to its small polarizability; the measured cross section is just about twice the hard sphere. For the SO_2 collider, on the other hand, the long range interaction is expected to be much more effective due to the availability of vibration-vibration transfer channels through transition dipole interactions. Indeed, in this case the measured cross section is almost 20 times larger than the hard sphere.

The huge cross sections have demonstrated that collision relaxation of highly excited molecules is quite different in nature from that of molecules excited with much lower energy. Highly excited molecules, with the possibility of rotation-vibration coupling for efficient rotational relaxation, high level density to relax the resonance condition for effective interaction through transition dipoles, and vibronic coupling to enhance the transition dipole, entice significantly larger cross sections for defining a relaxation collision. The new measurements indicate that, to consider how much energy is removed per collision for a highly vibrationally excited molecule, a cross section much larger than even the L-J cross section should be used. They also raise the question of whether energy transfer from a highly vibrationally excited molecule involves mainly large-quantity energy removal collisions or smaller-quantity collisions but with higher frequencies?

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