FAR WING RADIATION FROM ATOM-MOLECULE COLLISIONS

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The study of collisional lineshapes has concentrated so far on atom-atom collisions, especially on elastic atom-atom collisions. However, many interesting collision processes occur in atom-molecule collisions and in inelastic collisions. In particular, energy transfer processes such as electronic-to-vibrational, rotational and translational, and electronic-to-electronic are of great interest. Chemical reactions are perhaps the most important inelastic atom-molecule collisions. The study of chemical reactions, with detailed spectral information regarding the collision complex, is certainly one of the most fascinating possibilities envisioned for the application of collisional lineshapes. Polanyi and his collaborators [1] are already studying such processes. In the present talk I would like to discuss how the theory of line-wing shapes and atom-atom collisions can be expanded to the topic of atom-molecule collisions. I will then go on to discuss the particular example that we are studying in our laboratory, which is the electronic-to-vibrational energy transfer process of an excited sodium atom colliding with nitrogen or hydrogen molecules. The discussion of this example should bring out both the strengths and difficulties encountered in applying the collisional theory of lineshapes to the atom-molecule collision.

The classical Franck-Condon principle (CFCP) allows major simplification of the relationship between the spectrum and the interatomic potentials. In the two-body case, we are familiar with the strengths of this approximation as well as its weaknesses. These certainly carry over into the

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triatomic collision complex, but with the added complication that in triatomic collisions there are three coordinates that describe the interatomic interactions, compared to only one for the two-body case. As a result, it is inevitable that we have less uniqueness in analyzing the detected spectrum to obtain the interatomic potentials. However, as should become clearer in the example, one can gain a great deal of information regarding the triatomic interactions in spite of this lack of uniqueness.

An example of the CFCP for triatomic interactions is shown diagrammatically in Fig. 1 versus two of the coordinates related to the triatomic interaction. We have shown here only a single isolated pair of potentials, whereas much of the complication for the triatomic case arises because there are often several different molecular states from each separated atomic state. There are also many more regions of the three-coordinate space that have to be considered in calculating the entire spectrum. Furthermore, many of these regions of three-coordinate space will often produce the same wavelengths in emission or absorption. A further, very serious complication, is that in the inelastic collision case we cannot assume an equilibrated distribution of nuclear motion in an emission experiment. As a consequence we believe that it is essential to have theoretical potentials for use in analyzing any experiment involving

Fig. 1. Diagram of the classical Franck-Condon principle for a triatomic collision complex. The $R_1$ and $R_2$ dependence of an excited state and a ground state potential are shown for fixed $\theta$. 
triatomic, if one is going to draw any significant conclusions from the data. However, we hope to show here that continuum intensities are still a very powerful and interesting diagnostic of collisional interactions and collision processes in these more complicated situations.

The Na-N₂ electronic-to-vibrational energy-transfer process is a very well-studied process, both experimentally [2] and theoretically [3]. We have chosen to study the absorption and emission of this collision complex using two experimental methods, described in Fig. 2 where a diagram of the experimental arrangement is shown. For equilibrated vibrational-state distributions the spectrum observed by scanning the laser can be related by

Fig. 2. Diagram of the experimental measurements. In the method represented by the lower-left inset the laser frequency λₐ is scanned and Na fluorescence at λ₀ is detected. In the second method (lower-right inset) the laser, of frequency λ₀, excites free Na* and the emission spectrum λₛ is scanned.
simple Boltzmann and $v^3$ factors to that observed scanning the spectrometer. However, this is not the case here, due to the quenching of the excited electronic state by nitrogen. This quenching results in a very underpopulated bound-state distribution of the excited Na-N$_2$ molecular complex. In fact, we believe that a third measurement would be a very valuable complement of the two shown in Fig. 2, although we have not carried this out in our own laboratory. This would be a temperature-dependent absorption coefficient measurement of the same triatomic molecule, which would yield data corresponding to an equilibrated vibrational distribution of the Na$^*$-N$_2$ complex.

The type of data that we have obtained from the spectrometer-scan experiment is shown in Fig. 3. There is a rather striking feature of these data, which is that the entire red wing is essentially pressure-independent and temperature-independent, although it does show a different spectrum between

![Graph showing temperature dependence of normalized fluorescence spectra of Na(3P) in N$_2$ gas.](image)

**Fig. 3.** Temperature dependence of the normalized fluorescence spectra of Na(3P) in N$_2$ gas. The long-wavelength wing of the D lines has also been found to be independent of N$_2$ pressure from 10-500 Torr.
the two modes of the experiment; the laser-tuning as opposed to the spectrometer-tuning mode. The blue wing, on the other hand, is highly temperature-dependent and this yields the usual excellent diagnostic of the interatomic potentials.

For analysis of these data we first show in Fig. 4 the three-body potentials of Habitz [3] for the ground and first excited state of Na-N$_2$, in a projection of the coordinates $r$, the spacing between the nitrogen atoms, and $R$, the distance from the center of the N$_2$ molecule to the sodium atom. These potentials are shown for an angle $\theta$ between the nitrogen axis and the nitrogen-sodium axis of 90°, as shown in the Fig. 4 inset. This angle is believed to be the most important for the quenching process, and as a consequence Habitz has given the most potential information for this case. In Fig. 5 we show this same A-state potentials vs. the $r$ and $R$ coordinates, for $\theta = 90°$, but this time as a potential surface. Here we have also shown the potential difference between the A and X states. According to

![Diagram showing cross sections through Na-N$_2$ A-state and X-state potential surfaces, for $\theta = 90°$. Definitions of the coordinates $r$ and $R$ are shown in the insert.](image-url)
Fig. 5. The Na–N₂ A-state potential, for θ = 90°, is shown as solid lines. The potential difference identified with the photon energy, $V_A - V_X$, is shown as dashed lines.

the CFCP this difference-potential is equivalent to the photon energy radiated at the coordinate position shown. In Fig. 6 we show the R dependence of all of the potentials of the four states that separate to the ground and first excited state of sodium in the presence of nitrogen. Here we label these states X, A, A' and B according to their energy positions for θ = 90° and $r = 2.07 \ a_0$. Again we have chosen only the 90° angle to show these potentials, plus restricting $r$ to the equilibrium spacing of the N₂ molecule ($r = 2.07 \ a_0$). This is the $r$ coordinate that is most important in the problem since the nitrogen atoms have the highest probability of being near this coordinate spacing. In Fig. 7 we show variations in the potential differences vs. angle for $r = 2.07 \ a_0$.

To calculate a spectrum from these potentials we wish to use the CFCP in combination with a population-distribution in the three-coordinate space. The nitrogen remains primarily in its ground vibrational state prior to
Fig. 6. $V_B$, $V_A$, $V'_A$, and $V_X$ for $\theta = 90^\circ$ and $r = 2.07$ a$_0$, from the calculation of Habitz. The dashed lines are the potential differences $V_B-V_X$, $V'_A-V_X$, and $V_A-V_X$.

the absorption or emission of the photon. Consequently, we describe its population distribution in the r coordinate as that of the ground vibrational state of nitrogen in the local potential at a particular value of R. This is shown diagrammatically in Fig. 8. For the probability of sodium being at a coordinate R and an angle $\theta$ we will choose two distributions for comparison to the data. One of these will be an equilibrium distribution and the second will be essentially a free-particle collision distribution in which no bound states or quasi-bound states of the sodium nitrogen complex are present. We believe that this equilibrium distribution would not occur in an emission experiment, but it makes an interesting comparison to see how the spectrum of this distribution differs from that of the non-equilibrium distribution. In addition, a ground-state equilibrium distribution should apply in the absorption experiment and the resulting absorption spectrum is related to the equilibrium emission spectrum by a simple factor.
Fig. 7. Angular dependences of the potential differences $V_B - V_X$, $V_A^r - V_X$, and $V_A - V_X$.

The following equations are used for calculating the spectrum subject to either distribution. For a single $\alpha \rightarrow X$ emission band

$$I_\alpha(v) = [Na^*][N_2] P_\alpha(R, r, \theta) \Gamma_\alpha(R, r, \theta) \frac{d}{dv} \text{Vol}(R, r, \theta) \alpha$$

where

$$d\text{Vol} = 4\pi r^2 dr 2\pi R^2 dR \sin \theta d\theta$$

$\Gamma$ is the spontaneous emission rate which we assume to be $(v/v_o)^2 \Gamma_{\text{Atomic}}$, and

$$P_\alpha(R, r, \theta) = P_{N_2}(r-r_m) R, \theta P_{Na^*}(R, r_m, \theta)$$

is assumed. The $N_2$ distribution is assumed to be that of the vibrational motion in the $V_\alpha(r)$ potential for fixed $R$ and $\theta$. This is approximately
Fig. 8. A-state probability distribution $P_{N_2}(r,R)$ of the $N_2$ spacing $r$ when the Na distance is $r = 4.8$ or 7.5 $\lambda_p$.

\[ P_{N_2}(r-r_m)_{R,\theta} = \exp \left\{ \frac{V(r) - V(r_m)}{kT} \right\} \tag{2} \]

where $V(r)$ is the $\alpha$ potential for fixed $R$ and $\theta$. The $N_2^{-}$ distribution in $R$, for $r = r_m$, is given for an equilibrium distribution by

\[ P_{Na^{-}}(R,r_m,\theta) = \frac{g_\alpha}{g_{\text{Atom}}} \exp \left\{ \frac{V(R) - V_\infty}{kT} \right\} \tag{3} \]

where $V(R)$ is the $\alpha$ potential for $r = r_m$ and $\theta$. For free-particle $Na^{-}$, interaction $P_{Na^{-}}(R,r_m,\theta) = 1$ in the regions of attraction. The $\alpha$ line intensity is

\[ I_\alpha(v) = 4\pi r^2 \int_0^{\pi/2} \sin \theta \int_0^\infty \frac{P_{N_2}(r)}{\sqrt{dr/\sqrt{dv/d\theta}}} \left\{ \frac{2\pi}{3} \right\} \tag{4} \]
Here the expression in square brackets is the normalized $N_2$ distribution. If this is collapsed to $\delta(r_m)$ and the $\theta$ dependence of $V(r, R, \theta)$ is neglected, Eq. (4) reduces to the diatomic formula $I(\nu) = 4\pi R^2 |\nu|^{-1} P_{\nu}(R)$.

An important simplification occurs in evaluating this expression for the cases of the A' and B states. Specifically, the potential differences $V_{A'} - V_X$ and $V_B - V_X$ do not depend very strongly on the nitrogen coordinate $r$. Consequently, we can approximate the calculation by fixing the nitrogen spacing at the equilibrium distance $r = 2.07 \, a_o$ and the $\int dr[...]$ in Eq. (4) reduces to 1. In the A state, on the other hand, the interaction becomes much more attractive for larger values of $r$, as can be seen in Fig. 5. In fact, $V_X$ and $V_A$ cross in the neighborhood of $R = 3.7 \, a_o$, and it is to this that Habitz attributes the quenching process. Consequently, for the case of the A-X radiation we have evaluated the full expression in Eq. (1) and compared this to the approximation of fixing the nitrogen spacing at $R = 2.07 \, a_o$. We find that using the full nitrogen distribution produces a 20 to 50% increase in the intensity in the red wing as $\lambda$ increases from $\sim 620$ to 820 nm. (A larger change occurs in the equilibrium distribution, due to the deep binding of the A state at large values of the nitrogen spacing, $r$.) However, this change is smaller for other angles $\theta$, so that the effect on the final, angular-averaged spectrum is generally less than 20%.

The next averaging in the Eq. (1) process must be done over the angle $\theta$ even once we fix the coordinate $r$. Using the potential differences in Fig. 7, and potentials not shown there, we have done this average. We show the resulting free-Na and equilibrated-Na spectra for several values of $\theta$ in Fig. 9. We do this for all three bands, the B-X, A'-X, and A-X. The angular average of these bands is then taken by weighting these $\theta$ distributions according to the Simpson rule in cos $\theta$ space, since the integral in Eq. (1) is over cos $\theta$ from minus 1 to 1. This yields a $1/8:3/8:3/8:1/8$ weighting of the angles 0, 45, 70, and 90°. The results of these weighted sums are then shown as the angular averaged spectrum for the A-X,
Fig. 9. Normalized emission, in relative units, of the B-X, A'-X, and A-X bands for the θ angles given. The Na-N$_2$ distribution $P_{Na}(R)$ of Eq. (1), is I, corresponding to free-collision states, in the cases labeled $I^F$, and equilibrated in the cases labeled $I_{Equil}$.

A'-X and B-X bands, as illustrated in Fig. 10. The composite of these bands can be compared to the data in Fig. 3. It is important to note that in spite of this angular average, the A-X, A'-X and B-X bands each dominate one spectral region, and that the observed spectrum in each region is dominated by a particular range of angles.

Since the nitrogen distribution is basically that of the ground vibrational state, or in the case of the A'-X and B-X bands simply that of a fixed nitrogen spacing, and since the sodium distribution represents free-particle collision only, there is no temperature dependence to the red wing in
Fig. 10. Calculated Na-N₂ normalized emission spectrum, after angular averaging from Habitz potentials. The I^F and I^Equil labels are as in Fig. 9.

This calculated spectrum. This, of course, agrees with the experimental results, as it had to since we were taking distributions independent of temperature. The actual spectrum, however, does not agree with that measured on the red wing (Figs. 3 and 10). Since we do not see any temperature- or pressure-dependence it is hard to point definitively to any single cause of this discrepancy between the theoretical spectrum and the experimental one on the red wing. It is for this reason that an absorption experiment, with large equilibrium temperature dependences, would be a very valuable additional diagnostic. Nonetheless, it is apparent that larger V_A-V_X and V_A'-V_X are required. On the blue wing, on the other hand, both the measurements and the calculation show similar temperature-dependence, since here the sodium-nitrogen interaction is repulsive and the free-collision Na-N₂ states in fact represent the full equilibrium distribution of states. One can see that the exponential dependence upon temperature at each r,R,θ coordinate is largely preserved in the full spectrum in spite of the average over the angle 0 and the coordinates r
and R. This occurs because the theoretical $V_B - V_X$ is relatively independent of 0 and r. This is an example in which the spectrum remains a unique and valuable diagnostic of the interatomic potentials, as may be expected to occur in many instances of atom-molecule interactions.

In conclusion, we note that the radiative analysis of this atom-molecule collision is a good deal more complicated than that of an atom-atom collision. Nonetheless, the far wing emission or absorption spectrum can be analyzed from potential surfaces with relative ease using straightforward calculations. Furthermore, the spectra do give very detailed and powerful constraints upon the potentials even in this case where there are no clear satellites or features in the far wings. This is only our first attempt to apply CFCP-lineshape theory to atom-molecule collisions and we believe it has already been very informative. The importance of this class of collision problems clearly justifies further efforts in these directions.

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References


