

Characterization of vibrational overtones and "local" modes by emission spectroscopy

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(Received 2 April 1979; accepted 18 April 1979)

The concept of local modes in polyatomic molecules has recently been under examination, both theoretically¹⁻⁵ and experimentally.⁴⁻⁷ Bond locality has direct relevance to various interesting phenomena such as multiphoton dissociation of molecules and laser-induced chemistry. The characterization of local vs normal modes in moderate-sized molecules has recently been addressed theoretically by Gelbart and his group.^{1,2} Experimentally, the question

of local vs normal modes in liquids,⁵ gases,⁶ and cooled solids⁷ has been dealt with by observing the absorption spectra of the different overtones. A plot of $\Delta E v^{-1}$, the energy divided by the vibrational quantum number v , vs v gives a straight line consistent with (but not proof of) the idea of a simple Morse oscillator. These experimental results have been confined mostly to the CH stretch in molecules.

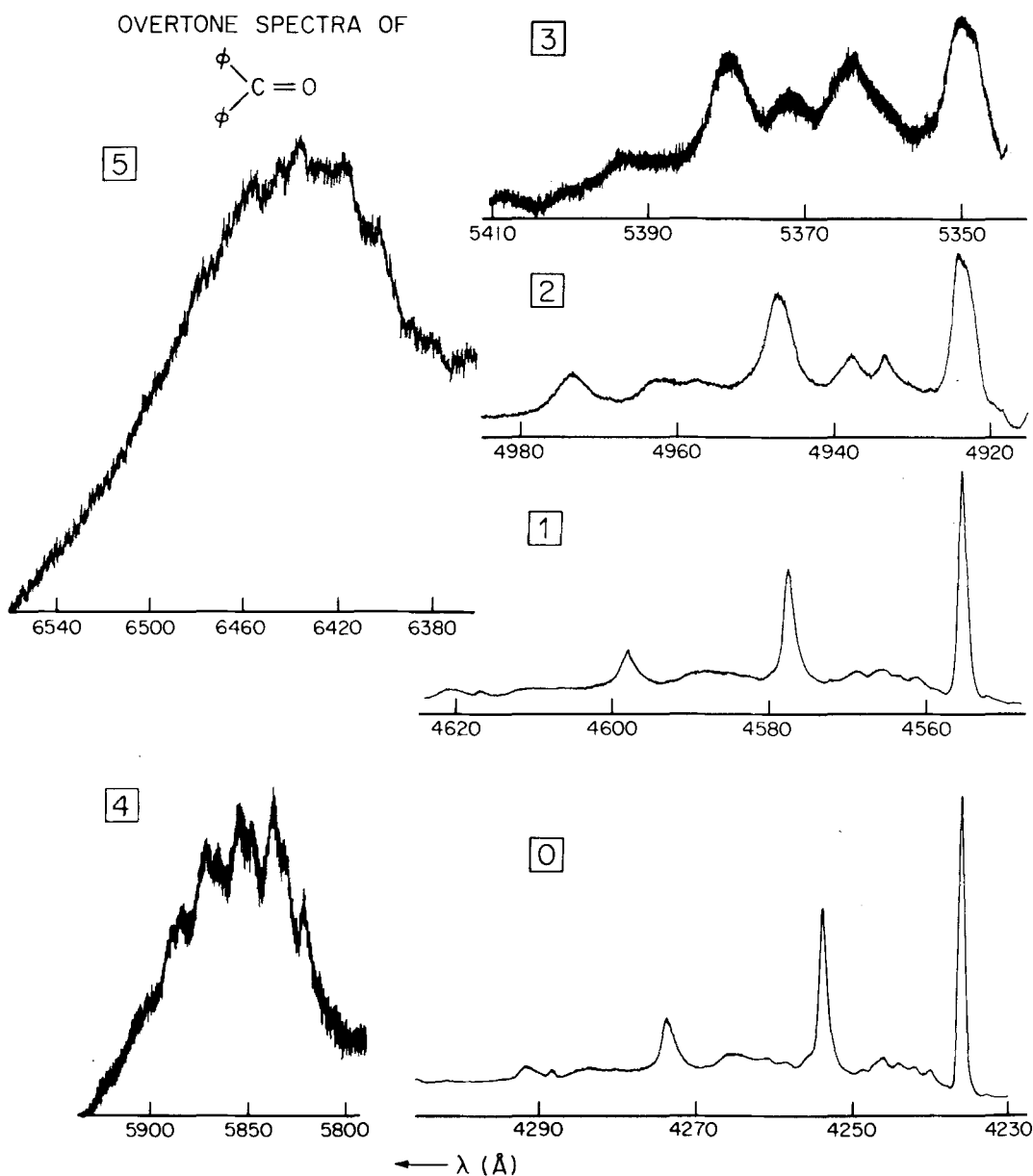


FIG. 1. The overtone spectra of benzophenone in DDE at 2 K. The numbers in boxes denote the CO vibrational quantum number. Note the broadening and the shift of the CO and torsional bands. The $v = 1$ line is an uneven doublet, and relative intensities are resolution limited.

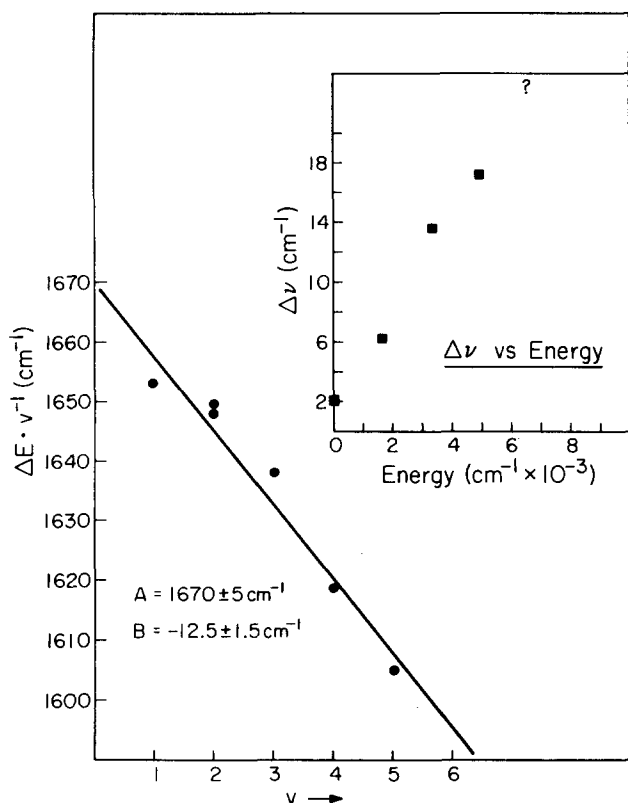


FIG. 2. A plot of $\Delta E v^{-1}$ vs v for benzophenone (CO stretch) in DDE at 2 K. The straight line is a linear least squares fit (see also footnote 9). The point for $v=1$ seems to be at lower $\Delta E v^{-1}$ than predicted by the best straight-line fit. However, our uncertainty at the moment is large. The insert is a plot of the apparent width, $\Delta\nu$, vs the energy of excitation. The 6477 cm^{-1} point is uncertain because of spectral overlap, and the width of $v=1$ includes the shoulder.

In this Communication, we use *emission* spectroscopy instead of absorption, as used in all previous work, and we explore a different type of molecule that may be useful for detailed theoretical inspection. The idea is quite simple—using a high-sensitivity spectrophotometer (e.g., one that utilizes photon counting) one scans the optical emission spectrum (say, the singlet-triplet transition) that has ground state vibrational overtones as final states. Knowing the energy of the 0,0 transition, one can deduce the energy of the mode as a function of v along with the *anharmonicity* and *transition linewidths*. Because we are using the emission and not the absorption (which requires long path lengths and/or dense media), several advantages can be realized. First, mixed crystals at low temperatures (or molecules in molecular beam nozzle sources) can be studied with very small concentrations (10^{-4} – 10^{-6} mol/mol) thus avoiding possible intermolecular perturbations (or in the case of a beam, collisional effects). Second, polarization techniques can be used to assign bands. Third, measurement of linewidths can be done easily, since the v transitions will be in the visible, as opposed to absorption measurements where IR detection is required in the low energy region. The method, however, relies on a finite and useful value for the Franck-Condon factor between the upper vibronic state and the

ground one.

The system studied here is benzophenone isolated in 4,4'-dibromodiphenyl ether at approximately 2 K. These mixed crystals exhibit a "clean" spectra consisting of a carbonyl (CO) progression together with (presumably) torsional modes of the two phenyls. The $v=1$ and 2 transitions of the carbonyl moiety have been characterized before.⁸ The crystals were grown from the melt by standard Bridgman techniques. The details of the spectrophotometer will be published elsewhere. All the work reported here utilizes the phosphorescence.

Figure 1 displays the overtone spectra of the benzophenone CO stretch at 2 K. (The detection sensitivity was enhanced approximately 10^4 to observe $v=5$; but note that the concentration of benzophenone was only about 10^{-4} M.) From the spectra we have learned several things; (a) When $\Delta E v^{-1}$ vs v is plotted for the CO overtones, we obtain a nearly straight line (see Fig. 2); (b) as one goes to higher overtones of CO, the apparent linewidth increases. In fact at $v=5$, all lines (CO and torsional) overlap, yielding a much broader resonance (CO width greater than 20 cm^{-1}); (c) the torsional progression exhibits a similar trend in linewidth with increasing quantum number.

From the plot of $\Delta E v^{-1}$ vs v , we find a fundamental frequency of $1670 \pm 5 \text{ cm}^{-1}$ and an anharmonicity constant of $-12.5 \pm 1.5 \text{ cm}^{-1}$.⁹ These data raise an interesting point. Probably due to the electronic excitation being highly localized on the CO,⁸ the progression in the ground state appears to have the nature of a "local" mode with appreciable diagonal anharmonicity. This suggests that the extent to which these modes couple to other modes should be evident from the line broadening as v increases. For $v=5$, an experimental estimate of the linewidth will be on the order of 50 cm^{-1} .¹⁰ It is perhaps accidental that this width is approximately half that of the naphthalene (100 cm^{-1}) $v=5$ transition of the CH stretch and that the ratio of the CH stretch frequency to the CO frequency is 1.85. In benzophenone, the torsional mode may prove to be the accepting mode for energy relaxation. This would be an example of vibrational relaxation due to the forces imposed on the CO by the neighboring CC bonds. As suggested by Shobatake *et al.*,¹¹ this kind of interaction yields a relaxation rate linear in v (see Fig. 2). However, one must first demonstrate the homogeneity of the overtone resonances and measure the contribution of pure dephasing to the linewidth before deducing the energy relaxation rate accurately from the line shape.¹²

In conclusion, by using simple optical techniques one can obtain the widths, the anharmonicity, and the energies of the high energy overtones. Comparison between absorption and emission data on linewidths and energies will be extremely important tests for current theoretical work. Finally, benzophenone offers an opportunity to unravel some of the "local" mode relaxation processes because of the apparent "two mode spectra" of the matrix-isolated molecule. Extension of these ideas to CH modes and to molecules in beams will be reported later. Similar to emission, Raman scattering into overtones should also be feasible.

This work was supported by a grant from the National Science Foundation.

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⁹From another set of data we obtained $1672 \pm 6 \text{ cm}^{-1}$ and $-14 \pm 2 \text{ cm}^{-1}$. These uncertainties are due to the broadening of the high-energy overtones and the error in the baselines.

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How symmetric stretch excitation in a triatomic molecule can be more efficient than asymmetric stretch excitation in enhancing reaction rates in atom plus triatom reactions

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We shall show how excitation in the *symmetric* stretch mode of a linear triatomic molecule can more efficiently lower the reaction threshold (and hence the activation energy) for many atom plus triatom reactions of the type $A + BCD \rightarrow AB + CD$ than a comparable amount of excitation in the *asymmetric* stretch, even though the transition state geometry is such that the BC bond is extended and the CD bond contracted. This effect will be illustrated using trajectory results for a collinear model of $O(^3P) + CS_2 \rightarrow CS + SO$.

The influence of reagent vibrational excitation on reaction rates has been of significant interest in the last few years,¹ especially in laser chemistry applications, and is now fairly well understood experimentally¹ and theoretically² for atom-diatom systems. For reactions involving triatomic molecules, the situation is much less certain, with only a few experiments reported in which the specific mode responsible for an enhancement has been studied.^{1,3,4} Occasionally it has been assumed that asymmetric stretch excitation should be most efficient in lowering the reaction threshold,⁵ although no theoretical studies of this point have been reported previously.

Consider the collinear atom plus linear triatomic molecule reaction $A + BCD \rightarrow AB + CD$, where atoms B and D are identical. The highest frequency mode of the reagents is normally the asymmetric stretch, and if the mass of atom C is much less than that of B or D, the difference between symmetric and asymmetric stretch frequencies can be quite large. At the transition state,

usually one of the two stable normal modes (here denoted ν_3) corresponds primarily to CD stretching (the "old" bond). If ν_3 is higher in frequency than the other stable mode (ν_1), then by the noncrossing rule ν_3 must correlate (in a vibrationally adiabatic sense) to the highest frequency mode of the reagents, i.e., the asym-

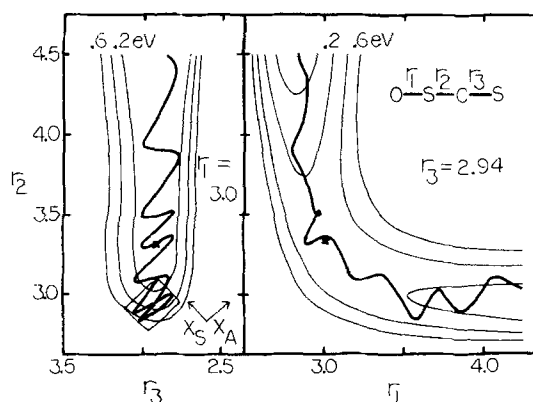


FIG. 1. Two cuts of the potential energy surface for $O + CS_2$, one at constant r_1 and one at constant r_3 . (See label in Figure.) All distances are in bohr, and the location of the saddle point is indicated by a cross. Contour energies given are relative to a zero of energy at the bottom of the CS_2 potential well with the O atom at infinite separation. A typical reactive trajectory for $O + CS_2(000)$ at $E_0 = 0.23 \text{ eV}$ (total energy = 0.37 eV) is projected onto these cuts. A "box" indicates caustics of the CS_2 vibrational motion prior to the collision. The directions of the symmetric and asymmetric stretch normal coordinates (in r_2, r_3 space) are labelled X_S and X_A , respectively, in the figure.