the simultaneous recording of this spectrum and that of the scattered laser light. The deviation of the center of the spectrum from the laser frequency is within the Fabry-Perot-interferometer width of 2 MHz.

Although none of the theories predicts any asymmetry in the heights of the side peaks, we have observed a slight, but reproducible, asymmetry.[12] The low-frequency peak was consistently smaller than the high-frequency peak by about 5-10%. A similar, but more severe, asymmetry has been observed by Schuda, Stroud, and Hercher[3] and Walther.[4] The effect of neighboring hyperfine levels may be eliminated by a scheme suggested by Abate[13] for the preparation of atomic sodium as a two-level system.

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[1] B. R. Mollow, Phys. Rev. 188, 1969 (1969).

[2] C. Cohen-Tannoudji, in *Proceedings of the Second Laser Spectroscopy Conference, Megève, France, 1975* (Springer, Berlin, 1975). This paper contains an extensive list of references.

[3] F. Schuda, C. R. Stroud, Jr., and M. Hercher, J. Phys. B: At. Mol. Phys. 7, 198 (1974).

[4] H. Walther, in *Proceedings of the Second Laser Spectroscopy Conference, Megève, France, 1975* (Springer, Berlin, 1975).

[5] F. Y. Wu, R. E. Grove, and S. Ezekiel, Appl. Phys. Lett. 25, 73 (1974); R. E. Grove, F. Y. Wu, and S. Ezekiel, Opt. Eng. 13, 531 (1974).

[6] This alignment is not the one that gives the most fluorescence from the observed region. We calculated and verified that optical pumping to the $F=1$ ground state depletes the $F=2$ population in the maximum-field region by a factor of about 2.5 (for 920 mW/cm^2).

[7] V. Weisskopf, Ann. Phys. (Leipzig) 9, 23 (1931).

[8] H. M. Gibbs and T. N. C. Venkatesan, post-deadline paper presented at the Conference on Laser Engineering and Applications, Washington, D. C., 28-30 May 1975 (unpublished).

[9] In the weak-field case the spatial distribution of the fluorescence is the same as that of the laser intensity. Therefore the Doppler broadening is less than that determined by aperture geometry.

[10] G. Oliver, E. Ressayre, and A. Tallet, Lett. Nuovo Cimento 2, 777 (1971); E. V. Baklanov, Zh. Eksp. Teor. Fiz. 65, 2203 (1973) [Sov. Phys. JETP 38, 1100 (1974)]; H. J. Carmichael and D. F. Walls, J. Phys. B: At. Mol. Phys. 8, L77 (1975); S. S. Hassan and R. K. Bullough, J. Phys. B: At. Mol. Phys. 8, L147 (1975).

[11] Broadening from this effect is not as severe as might be expected, since optical pumping transfers most of the atoms into the $m_F = 0, \pm 1$ sublevels, which have approximately equal matrix elements for $\Delta m = 0$ transitions.

[12] This cannot be explained by fluorescence from the transition $F' = 2$ to $F = 1$ which we found negligible except for large negative detuning.

[13] J. A. Abate, Opt. Commun. 10, 269 (1974).

Vibrational Excitation in Benzene by Electron Impact via Resonances: Selection Rules*

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The vibrational excitation in the energy ranges of the lowest resonances in benzene has been measured and it is found that only few fundamental modes become excited. This selectivity of the excitation process can be understood in terms of selection rules which are based on symmetry considerations. The angular distribution of scattered electrons in the range of the lowest shape resonance (~1.2 eV) is consistent with an f_δ wave as the dominant partial wave.

In this Letter we present experimental measurements on the vibrational excitation in benzene (C_6H_6 and C_6D_6) by electron impact at low energies. We consider the experimental observations presented here as prototypes for similar processes in the larger molecules. In particular, we study the vibrational modes excited by electron impact in the regions of the lowest shape resonances at energies of about 1.2 and 4.8 eV. Despite the large number of fundamental vibrational modes in which the benzene molecule can vibrate, *only very few modes are observed.* In order to explain this selective excitation, we develop a set of *selection rules* for vibrational excitation via resonances. These selections rules are based on the symmetry of the resonances and a few additional, physically reasonable postulates.

We find that the angular distribution of electrons near 1.2 eV is dominated by an f_δ partial wave and thus we establish that the resonance near 1.2 eV is the lowest state of $C_6H_6^-$.

The energies of shape resonances (compound states) in benzene have been studied previously by electron transmission spectroscopy[1] and by other methods. The lowest resonance, $^2E_{2u}$, which consists of the neutral molecule plus an electron in the e_{2u} orbital, is doubly degenerate. The ground vibrational level of this compound-state system has been previously placed[1] at 1.15 eV and *higher vibrational levels of this compound state have also been observed, but will not be further discussed in this Letter.* The removal of the degeneracy of this state by substitution of nitrogen atoms is discussed in Ref. 1.

The "third" compound state is short-lived, as evidenced by a broad structure in electron transmission spectrum[1] (centered near 4.8 eV) without fine structure. This state, $^2B_{2g}$, consists of the benzene molecule in the ground state plus an electron in the b_{2g} orbital.

The compound states enumerated above decay by the emission of the extra electron, leaving the molecule in various modes of vibrational excitation. It is the purpose of this paper to describe the vibrational modes thus produced and to suggest the selection rules which govern the decay.

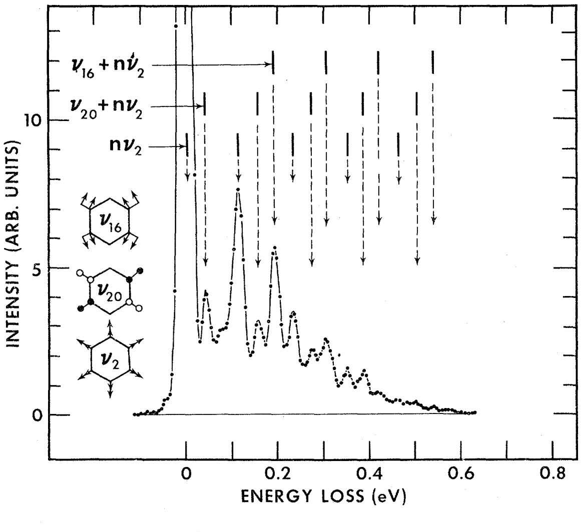

FIG. 1. Energy-loss spectrum in C_6D_6 at an incident energy of 1.18 eV (the ground vibrational level of the $^2E_{2u}$ resonance) and an angle of observation of 70°. Only the modes ν_2, ν_{16}, and ν_{20} (Herzberg's notation) become appreciably excited. The geometry of these modes is indicated. Only one each of the doubly degenerate modes for ν_{16} and ν_{20} are shown.

In the present experiment[2] we cross a molecular beam with a beam of monochromatic electrons in a hemispherical electrostatic analyzer, having a resolution of about 16 meV. The energy scale in the present experiment is determined with respect to the first peak in the vibrational excitation cross section ($v=1$) of N_2 at 1.97 eV,[3] by admixing a small amount of N_2 to the benzene vapor.

In Fig. 1 we show an energy-loss spectrum in C_6D_6 when the energy of the incident electron is fixed at 1.18 eV. This is the energy at which the vibrational excitation cross section exhibits its first sharp peak and we can loosely associate this energy with the $v=0$ level of the compound state. Bearing in mind that the benzene molecule possesses thirty normal vibrational modes (twenty fundamental frequencies), it is at first sight surprising that only the three fundamental modes shown in Fig. 1 have a large probability for being excited. In Herzberg's notation,[4] which is used throughout this paper, they are ν_2, ν_{16}, and ν_{20} with symmetries a_{1g}, e_{2g}, and e_{2u}, respectively.

Figure 2 shows the energy-loss spectrum in the center of the 4.8-eV resonances. The modes which we assign to the two prominent peaks are ν_1 (a_{1g}) and ν_7 (b_{2g}). Figure 2, just like Fig. 1, shows a dramatic selectivity in the excitation mechanism, which led us to the development of the selection rules outlined below.

The assignment of the modes in Figs. 1 and 2 comes not only from the position of the energy-loss peaks, but also from the isotope effect, i.e.,

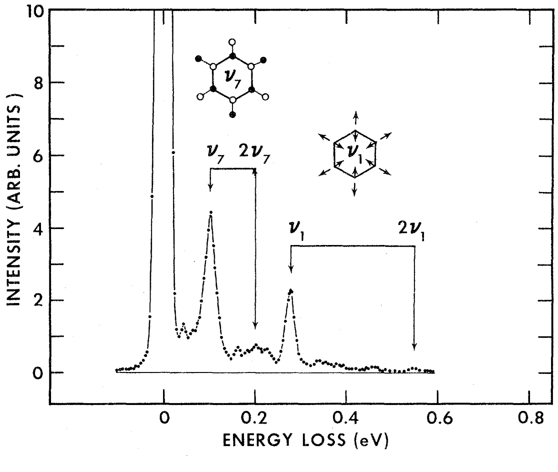

FIG. 2. Energy-loss spectrum in C_6D_6 at an incident energy of 4.8 eV (the center of the $^2B_{2g}$ resonance) and an angle of 70°. Only the modes ν_1 and ν_7 are appreciably excited.

the shift of a given energy-loss peak in C_6H_6 compared to C_6D_6.[4] We note that the energy-loss spectra in C_6H_6 are similar to those shown for C_6D_6, but subtle differences exist in the ratio of peak heights, especially for the less prominent peaks. The geometries of the modes which are prominently excited are indicated in Figs. 1 and 2.

It has already been pointed out by Bardsley and Read[5] that the $^2E_{2\text{u}}$ resonance is expected to occur predominantly in the f_δ partial wave. Thus, when we examine the angular distribution of electrons having excited the totally symmetric C-C stretch mode, ν_2 ($a_{1\text{g}}$), we should obtain an angular distribution characteristic of the f_δ partial wave. The angular distribution which we find experimentally for C_6H_6 in the angular range 25–100 deg is in fact reminiscent of an f_δ partial wave, with a clear minimum near 40 deg; the second minimum expected for f_δ partial wave at 90 deg is somewhat washed out. We consider the fairly good agreement between theory and experiment as a confirmation that we are dealing here with the first shape resonance of benzene and that no lower resonance or negative-ion state can exist, within our present understanding of the normal benzene molecule.[6] The deviation of the experimental curve from a pure f_δ wave may be attributed to the admixture of other partial waves, as will be discussed below.

In sharp contrast, the angular distribution of electrons which have excited infrared-active modes by nonresonant processes [e.g., ν_4 ($a_{2\text{u}}$)] is monotonic and exhibits a strong peak in the forward direction. The excitation of the ν_4 mode decreases monotonically with energy, without structure in the resonance regions.

The selectivity of the vibrational modes excited *via resonances* makes it clear that selection rules are in operation. These can be understood partly by the relation between the symmetries of the resonances involved and the symmetries of the vibrational modes: Vibrational modes can become excited only when the transition matrix element $\langle \chi_f | G | \chi_0 \rangle$ is nonvanishing. The symmetries of the nuclear wave functions χ_f (for the final vibrational mode) and χ_0 (for the initial vibrational mode) are specified by the symmetry representation of the appropriate normal modes. The symmetry of the propagator G (which can be replaced for our purposes by the interaction Hamiltonian) is characterized by the charge distribution of the extra electron and can be obtained by forming the symmetric product[7] of the representation of the resonant orbital.[8]

TABLE I. Vibrational modes excited via the 1.2-eV resonance in benzene. Selection rule: $f_\delta + s_\sigma +$ rigid constraint. Herzberg's notation is used for the designation of vibrational modes. ν_{19} and ν_{20} are out-of-plane modes.

	Symmetry							
	$a_{1\text{g}}$		$e_{2\text{g}}$				$e_{2\text{u}}$	
f_δ wave ($e_{2\text{u}}$)	ν_1	ν_2	ν_{15}	ν_{16}	ν_{17}	ν_{18}		
s_σ wave ($a_{1\text{g}}$)							ν_{19}	ν_{20}
Rigid C-H		×		×		×		×
Strongly obs.		×		×				×

We now apply these guidelines to the vibrational excitation via the 1.2- and 4.8-eV resonances. The transition matrix elements are evaluated with reference to D_{6h}, the point group of benzene.

(i) *Undistorted resonance.*—For the 1.2-eV resonance in benzene, the symmetry of the electron orbital, $e_{2\text{u}}$, leads to an electrostatic potential of symmetry $A_{1\text{g}}$ and $E_{2\text{g}}$. This allows the excitation of fundamental modes $a_{1\text{g}}$ (ν_1 and ν_2) and $e_{2\text{g}}$ (ν_{15}, ν_{16}, ν_{17}, and ν_{18}). These modes are listed on line 1 of Table I.

For the 4.8-eV resonance, the orbital has a symmetry $b_{2\text{g}}$, and G has a symmetry $A_{1\text{g}}$. This allows the excitation of the ν_1 and ν_2 modes. These are listed on line 1 in Table II.

(ii) *Out-of-plane distortion.*—It may not be unreasonable to postulate that the benzene ion has an incipient out-of-plane distortion (puckering). In order to explain our results in the simplest manner, we wish to consider that a component of $a_{1\text{g}}$ symmetry is admixed to the "undistorted" $e_{2\text{u}}$ orbital. This postulate, which is tantamount to adding an s_σ component to the scattered wave, allows us to predict additional allowed modes: These are ν_{19} ($e_{2\text{u}}$) and ν_{20} ($e_{2\text{u}}$) in the case of the

TABLE II. Vibrational modes excited via the 4.8-eV resonance in benzene. Selection rule: $g_\varphi + s_\sigma +$ nonrigid constraint. ν_7 and ν_8 are out-of-plane modes.

	Symmetry			
	$a_{1\text{g}}$		$b_{2\text{g}}$	
g_φ wave ($b_{2\text{g}}$)	ν_1	ν_2		
s_σ wave ($a_{1\text{g}}$)			ν_7	ν_8
Nonrigid C-H	×		×	
Strongly obs.	×		×	

1.2-eV resonance; for the 4.8-eV resonance the additional allowed modes are ν_7 (b_{2g}) and ν_8 (b_{2g}). These modes are listed on line 2 of Tables I and II. The s_σ component in the partial-wave expansion also could be responsible for the deviation from a pure f_δ wave in the angular distribution of electrons in the region of the 1.2-eV resonance.

(iii) *Rigidity of the C-H bond.*—In line 4 of Tables I and II we list those modes which are strongly developed in our energy-loss experiments. We note that in the case of the 1.2-eV resonance, only those modes are strongly observed which have a rigid C-H separation. In the case of the 4.8-eV resonance, only those modes are observed which have a nonrigid C-H bond. We can argue that the radial distribution of the extra electron may be responsible for this selection rule.[9]

Our findings are consistent with the viewpoint that the angular symmetry of the charge distribution sorts out the symmetry of the allowed vibrational modes. These can be subdivided into those in which the C-H bond is excited ("nonrigid modes") and those in which the C-H bond remains unexcited ("rigid modes"). It is the radial extent of the charge distribution in the resonance which controls which of these modes are preferentially excited. It is possible that the latter finding will lead us to a knowledge of the radial distribution of the charge cloud directly from experiments.

In addition to their intrinsic interest, the selective excitation mechanisms described above may be of importance in the understanding of chemical reactions taking place in gas discharges through hydrocarbon vapors. Also, the selectivity in vibrational excitation is a desirable property for inverting the vibrational population in gas lasers.

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[1] I. Nenner and G. J. Schulz, J. Chem. Phys. 62, 1747 (1975), and references contained therein.

[2] For a description of the apparatus, see M. J. W. Boness and G. J. Schulz, Phys. Rev. A 9, 1969 (1974).

[3] M. Eyb and H. Hofmann, J. Phys. B: At. Mol. Phys. 8, 1095 (1975), and private communication.

[4] G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, Princeton, N.J., 1967). For the values of the vibrational frequencies in C_6H_6 and C_6D_6 we have used L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Vibrational Spectra of Polyatomic Molecules* (Wiley, New York, 1974). See also G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives* (Wiley, New York, 1974).

[5] J. N. Bardsley and F. H. Read, Chem. Phys. Lett. 2, 333 (1968).

[6] This finding appears to be at variance with the results of swarm experiments by L. G. Christophorou and R. E. Goans, J. Chem. Phys. 60, 4244 (1974).

[7] A general method for obtaining the symmetric product of a representation with itself as well as other pertinent items of group theory can be found in L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Pergamon, Oxford, England, 1965), Chap. XII.

[8] This procedure is valid provided that the vibrational symmetry of the negative ion is totally symmetric with respect to the nuclear framework. For both cases considered in the text, this condition is fulfilled. For the 1.2-eV resonance we consider only the ***ground*** vibrational level; for the 4.8-eV resonance, the above condition is assured by the short lifetime of the resonance. A detailed account of these considerations is in preparation (S. F. Wong and W. C. Tam, unpublished).

[9] According to the Hellmann-Feyman theorem [for a review, see B. M. Deb, Rev. Mod. Phys. 45, 22 (1973)], the additional force acting on the nuclei of a molecule is specified by the charge distribution of the extra electron.