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Franck–Condon factors and autoionization in the photoelectron spectra of diatomic molecules

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Distributions of calculated Franck–Condon factors for autoionizing transitions are used to illustrate the way in which the vibrational structure of the photoelectron spectrum may be extended in a characteristic manner when the wavelength of the exciting radiation coincides with a resonance in the photoionization cross section of a diatomic gas. The calculations are found to be in good agreement with resonance wavelength photoelectron spectra from O₂.

INTRODUCTION

The photoelectron spectra of diatomic molecules consist, in general, of several bands which are resolved into a number of peaks, each of which corresponds to a transition from the initial state of the molecule to a particular electronic and vibrational state of the ion. The extent of the vibrational structure depends on the bonding character of the electron which is removed, and in many cases it has been found that the intensity distribution of the peaks in a band is closely related to the calculated Franck–Condon factors (see, for example, Turner & May 1966; Frost, McDowell & Vroom 1967). In some photoelectron spectra excited with radiation of wavelength coinciding with an autoionized resonance in the absorption cross section of the molecule, it has been noticed that the vibrational structure of a particular band is greatly enhanced and extended. The purpose of this paper is to discuss the appearance of these spectra in terms of the Franck–Condon principle.

FRANCK–CONDON FACTORS FOR PHOTOIONIZATION

For a diatomic molecule the probability of photoionization is given by:

$$I_{v'} = K_{e1} \nu q_{v'v''}; \quad q_{v'v''} = [\int \psi_{v'} \psi_{v''} dr]^2, \quad (1)$$

where $I_{v'}$ is the probability of a transition to the vibrational level v' of the ion, $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wavefunctions for the initial and final states of the ionizing transition, $q_{v'v''}$ is the Franck–Condon factor, K_{e1} is a factor which depends on the electronic transition probability and the statistical weight of the final state, and ν is the photon frequency. It is assumed that K_{e1} varies slowly with the internuclear distance r (Herzberg 1950).

In general $q_{v'v''}$ has a significant value for several values of v' for a given v'' , and we refer to these as a distribution of Franck–Condon factors. The form of this distribution depends largely upon the value of v'' and the change in equilibrium internuclear distance which occurs when the electron is removed. Several distributions of calculated Franck–Condon factors are shown in figure 1 for ionizing transitions between two typical electronic states whose potential energy curves have minima separated by an amount Δr_e . The height of each heavy vertical line represents the Franck–Condon factor for the transition from the vibrational level v'' of the molecule

to the level v' of the ionic state, and v' increases from right to left. Each distribution may be considered as a photoelectron spectrum, with the electron energy increasing from left to right.

For the case of direct ionization from the ground electronic state of the molecule at room temperature the value of v'' is restricted to zero. When Δr_e is very small, corresponding to the removal of a non-bonding electron, there is almost total overlap between the wavefunctions $\psi_{v''=0}$ and $\psi_{v'=0}$, and the $v' = 0$ level is excited strongly to the exclusion of others as shown in

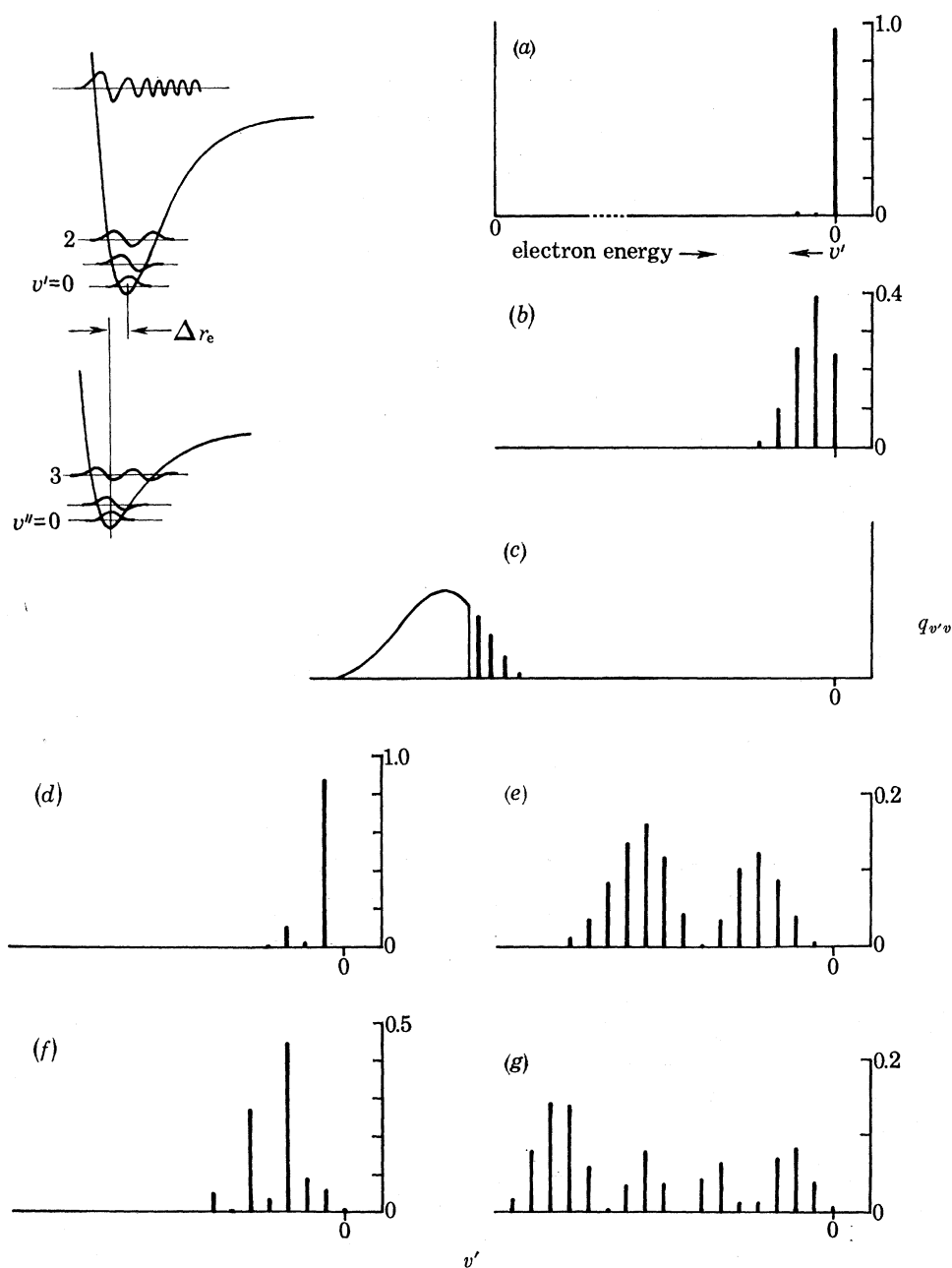


FIGURE 1. The potential energy curves with vibrational levels v'' and v' indicate the initial and final electronic states of ionizing transitions in a diatomic molecule which result in a change Δr_e of the equilibrium nuclear separation. The Franck-Condon factors for transitions $v'' \rightarrow v'$ are represented by heavy vertical lines: (a) $v'' = 0$, $\Delta r_e = 0$; (b) $v'' = 0$, $\Delta r_e = 0.1 \text{ \AA}$; (c) $v'' = 0$, $\Delta r_e \approx 0.4 \text{ \AA}$; (d) $v'' = 1$, $\Delta r_e = 0$; (e) $v'' = 1$, $\Delta r_e = -0.2 \text{ \AA}$; (f) $v'' = 3$, $\Delta r_e = 0$; (g) $v'' = 3$, $\Delta r_e = -0.2 \text{ \AA}$.

figure 1*a*. As Δr_e increases $\psi_{v''=0}$ begins to have significant overlap with other wavefunctions $\psi_{v'}$, and the electronic transition probability is shared among several levels v' (figure 1*b*). For large values of Δr_e it may be expected that the discrete spectrum is joined by a continuous distribution corresponding to dissociative ionization, as shown in figure 1*c*. The form of observed photoelectron spectra do in fact behave in this manner.

If the gas is excited with radiation of a wavelength which coincides with an autoionized resonance in the absorption cross-section, then there is a large probability that the molecule is excited to the discrete state, which is a well defined vibrational level, and it then decays to the ionization continuum. It is reasonable to expect that the photoelectron spectrum resulting from autoionization is described by the distribution of Franck-Condon factors for the decay of the autoionizing state, and since the value of v'' is no longer restricted to zero more complex distributions of the Franck-Condon factors occur. For small values of v'' it is found that the distribution of $q_{v'v''}$ has $(v'' + 1)$ maxima, which correspond to overlap of the $\psi_{v'}$ with successive maxima of the function $\psi_{v''}$. Typical distributions for $v'' = 1$ and $v'' = 3$ are shown in figures 1*d* to *g*. They illustrate the way in which vibrational structure in photoelectron spectra may be dramatically extended as a result of autoionization in a way that is characteristic of the autoionizing level.

Complex spectra are reconstructed by combining the relevant Franck-Condon distributions, each weighted by a factor K_{e1} . The origin of the electron energy scale for each band is determined by the photon energy and the appropriate ionization potential. Using the vibrational sum rule:

$$\sum_{v''} q_{v'v''} = 1, \quad (2)$$

the sum of the strengths of the peaks in a band is proportional to K_{e1} for a given photon energy, and to the partial photoionization cross section corresponding to the particular electronic state of the ion. However, in some cases the distribution of Franck-Condon factors may extend below the zero of the electron energy scale as a result of autoionization, and the whole distribution will not be seen in the photoelectron spectrum.

RESONANCE PHOTOELECTRON SPECTRA

Photoelectron spectra resulting from autoionization in molecular oxygen have been recorded at wavelengths corresponding to several strong resonances in the absorption cross-section. The gas was excited with helium Hopfield continuum radiation dispersed with a scanning monochromator, and photoelectrons which passed through a spherically symmetrical retarding potential analyser were counted individually.

The spectra recorded at 885.8 and 839.1 Å are shown in the upper parts of figures 2*a* and *b*. These wavelengths correspond to the $v = 1$ member of the J progression and the $v = 2$ member of the I progression which are observed in the photoionization cross-section (Matsunaga & Watanabe 1967). At these wavelengths only the ${}^2\Pi_g$ ground electronic state of the ion is excited, but the vibrational structure due to this state is extended to the threshold of the spectra. In both of the spectra the strength of the structure has $(v + 1)$ maxima, where v is the vibrational quantum number of the autoionizing level.

The spectra are compared with Franck-Condon factors for autoionization which were calculated using the Morse potential function. These are plotted in the lower parts of figures 2*a* and *b*, where the dashed lines represent the parts of the Franck-Condon distributions which

are not observed in the spectra. The calculations were fitted to the spectra by varying the values used for the equilibrium internuclear distance of the I and J states of O_2 . Optimum values for r_e were 1.35 and 1.30 Å respectively. The experimental method and the spectra will be described in more detail in another paper.

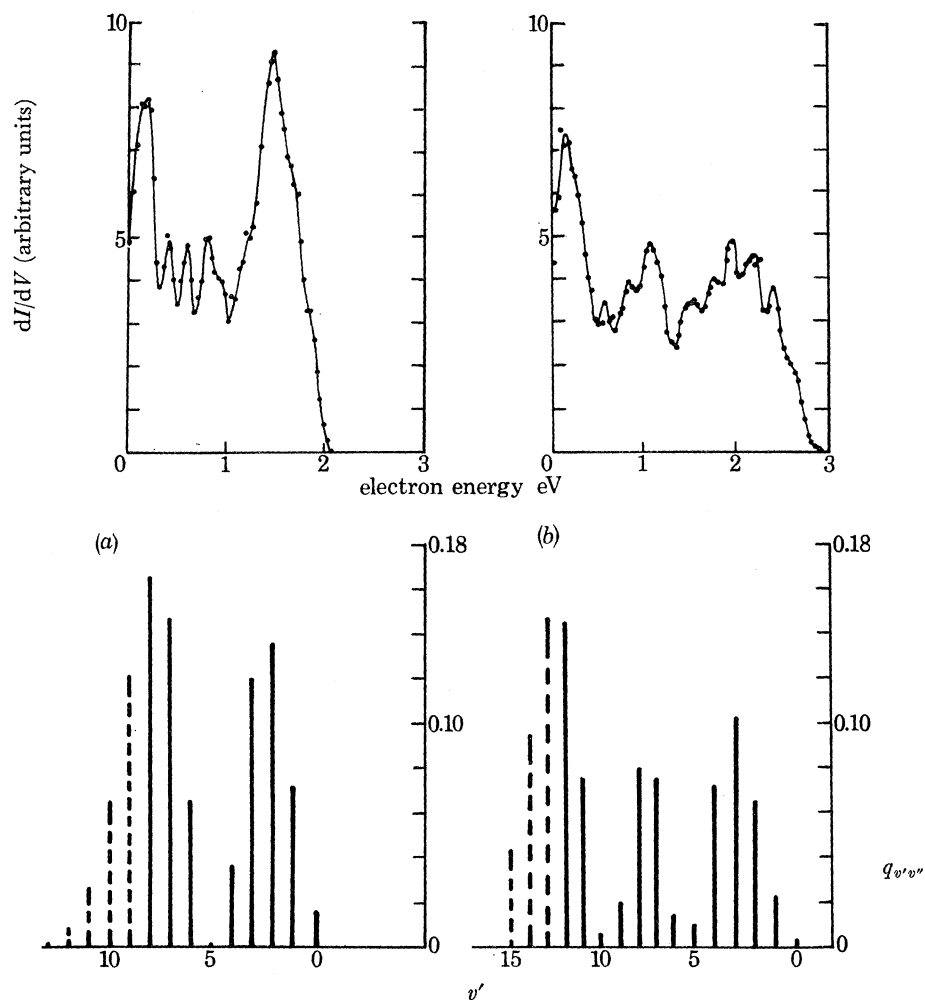


FIGURE 2. Resonance wavelength photoelectron spectra from O_2 and the corresponding distributions of Franck-Condon factors for autoionization. (a) 885.8 Å resonance (J progression, $v'' = 1$); (b) 839.1 Å resonance (I progression, $v'' = 2$).

It is apparent that the extended vibrational structure in these resonance wavelength spectra is explained by the overlap between the vibrational wavefunctions. In cases where the photoelectron spectrum has a form which is characteristic of the autoionizing state, a comparison of the spectrum with calculated Franck-Condon factors provides useful information about the autoionizing state.

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