The Role of Autoionization in Molecular Photoelectron Spectra

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The role of autoionization in molecular photoelectron spectra

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The Fano–Mies theory of configuration interaction is applied to the photoionization of diatomic molecules, yielding an expression which gives the relative intensity of vibrational peaks in photoelectron spectra when one or more autoionizing states are in the vicinity of the excitation energy. In some cases the vibrational intensity distribution depends only on Franck–Condon factors connecting autoionizing and final states. Illustrative calculations for O_2 show the transition from this limit to the limit of direct photoionization as the line profile index decreases.

1. INTRODUCTION

Relative intensities of resolved vibrational peaks in molecular photoelectron spectra are usually assumed to be proportional to the Franck–Condon factors connecting the molecular ground state with the molecular ion final state. Recent experiments have shown, however, that the photoionization of O_2 with radiation whose energy lies close to autoionizing states (either the neon resonance lines (Price 1968; Natalis & Collin 1968) or monochromatic excitation right at a strong autoionizing peak in the absorption spectrum Blake *et al.*, this volume, p. 159) produces $O_2^+(X^2\Pi_g)$ with vibrational populations departing strongly from those expected from calculated Franck–Condon factors (Nicholls 1968) for the ionizing transition. These anomalous vibrational intensities also occur in the photoelectron spectra of other molecules (Collin & Natalis 1968*a*) and complicate attempts to identify electronic energy states of the respective molecular ions (Collin & Natalis 1968*b*; Huber 1968).

In this paper the effect of autoionization on photoelectron spectra is explored by applying Fano's configuration interaction theory (Fano 1961; Fano & Cooper 1965, 1968) to molecular photoionization. Using the recent extension of the theory by Mies (1968) an expression is derived for the intensity of a vibrational peak in the photoelectron spectrum when there are one or more autoionizing Rydberg states in the vicinity of the excitation energy. The theory is more general than that developed by Bardsley (1968) for the analysis of molecular resonances but reduces to his results in the limit of a single autoionizing state. As an example (illustrative, not quantitative), the photoelectron spectra of O_2 (to $O_2^+(X^2\Pi_g)$) is calculated as the excitation energy sweeps through autoionizing Rydberg states leading to $O_2^+(A^2\Pi_u)$.

2. THEORY

Consider the direct photoionization of the ground state i of a diatomic molecule into a single molecular ion electronic state f with vibrational states α. The *total* photoionization cross-section at energy E is (Mies 1968)

$$\sigma_f = \sum_\alpha \sigma_{\alpha,f} = \sum_\alpha |t_\alpha^-|^2 = \sum_\alpha |\langle \Psi_{\alpha,f}^- | T | \Psi_i \rangle|^2, \tag{1}$$

where T is the dipole moment operator and t_α^- and $\sigma_{\alpha,f}$ are, respectively, the transition amplitude and partial cross-section into vibrational state α. With the Born–Oppenheimer

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approximation to factor the wavefunctions into an electronic and a vibrational part,† the transition amplitude into each final channel is a product of an electronic transition amplitude into the photoionization continuum, t^{C}, and a Franck–Condon *amplitude* $T_{i,\,\alpha}$:

$$\Psi_i = \Psi_i^{\mathrm{el}}\xi_i(R), \quad \Psi^{-}_{\alpha,f} = \Psi_f^{\mathrm{el}}\xi_\alpha(R), \quad E = E_\alpha + e_\alpha, \tag{2}$$

$$\begin{aligned} t_\alpha^{-} &= \langle\Psi_i^{\mathrm{el}}|T|\Psi_f^{\mathrm{el}}\rangle\langle\xi_i|\xi_\alpha\rangle \\ &= t^{\mathrm{C}}F_{i,\,\alpha}. \end{aligned} \tag{3}$$

Here E_α is the energy of state (f, α) and e_α is the corresponding kinetic energy of the photoelectron. If t^{C} is assumed independent of total energy and photoelectron energy, the intensity ratio of two vibrational peaks $(\alpha+1, \alpha)$ in the photoelectron spectrum is equal to the ratio of corresponding Franck–Condon factors from the molecular ground state:

$$\frac{\text{intensity }(\alpha+1)}{\text{intensity }(\alpha)} = \frac{F^2_{i,\,\alpha+1}}{F^2_{i,\,\alpha}}. \tag{4}$$

This relation has been assumed in previous studies which have deduced Franck–Condon factors from photoelectron spectral intensities (Turner & May 1966).

If there are discrete (neutral) states at or near the photon energy E, then the photoionization may proceed through these autoionizing or 'resonance' states, and the partial cross-section into each channel will be affected by the transition amplitudes to and from these resonance states.

For simplicity, assume that every autoionizing state is a Rydberg states leading up to an excited state of the molecular ion with vibrational states ν. The Rydberg state may be characterized by its effective principal quantum number $n^* = n-\delta$, where δ is the quantum defect, and by its vibrational state ν (assuming the same vibrational constants for the Rydberg state and the ion). Assume that the energy of the state $E_{\nu,\,n^*}$ is sufficiently high that it may autoionize to any of the vibrational states α of the final state f. Fano & Cooper (1965) have shown that

$$\sigma_f = \sigma_{\mathrm{a}}\frac{(q+\epsilon_{\nu,\,n^*})^2}{1+\epsilon^2_{\nu,\,n^*}} + \sigma_{\mathrm{b}}, \tag{5}$$

where

$$\epsilon_{\nu,\,n^*} = (E-E_{\nu,\,n^*})/(\tfrac{1}{2}\Gamma) \tag{6}$$

and

$$\Gamma = \sum_\alpha \Gamma_\alpha = 2\pi\sum_\alpha|\langle\Psi^{-}_{\alpha,f}|H|\Psi_{\nu,\,n^*}\rangle|^2. \tag{7}$$

Here Γ is the total autoionization width of state (n^*, ν) or $\hbar$ times the auotionization rate, with H the interelectronic repulsion causing the two-electron transition. The quantity q is Fano's 'line profile index', the sum $\sigma_{\mathrm{a}}+\sigma_{\mathrm{b}}$ is the photoionization cross-section in the absence of autoionization, and the ratio $\sigma_{\mathrm{a}}/(\sigma_{\mathrm{a}}+\sigma_{\mathrm{b}})$ is Fano's 'correlation coefficient' (Fano & Cooper 1965). From the definitions of these quantities and the Born–Oppenheimer factorization of (2), the following results emerge:

(1) The autoionization width is independent of vibrational quantum number ν and proportional to $(n^*)^{-3}$.

(2) The line profile index q is also independent of ν, and independent of n^* as well. The quantity $\frac{1}{2}\pi q^2$ now has a simple physical interpretation as the ratio of two electronic oscillator strengths: in the numerator, the oscillator strength to the discrete Rydberg state n^*

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† Molecular rotation is ignored in this work. Since photoelectron spectra do not normally resolve rotational structure there is not much incentive to develop a theory including rotational effects, particularly when one confronts problems such as the change of angular momentum coupling (Hund's case $b \rightarrow$ case d) as one goes up a Rydberg series or as rotational quantum number increases. Any detailed comparison of theory and experiment must await a full treatment of rotational effects, however.

(proportional to $(n^*)^{-3}$), and in the denominator the differential oscillator strength to the photoionization continuum of the final state f times the autoionization width of state n^*.

(3) The correlation coefficient is $F^2_{i,\nu}$, the Franck–Condon factor connecting the *initial* and *autoionizing state.*

(4) The ratio of the total photoionization cross-section at its maximum near a resonance ($\epsilon = 1/q$) to its value far from the resonance is $1+F^2_{i,\nu}q^2$.

These expressions of Fano & Cooper do not yield the partial cross-section into each state α in the presence of autoionization. Mies (1968) has extended Fano's theory of configuration interaction to include the case of many discrete states interacting with many continuum channels, with the possibility that neighbouring resonances may overlap, i.e. that their autoionization widths may be greater than the spacing between discrete states. Although the theory is more complicated than that proposed by Bardsley (1968) for analysing molecular resonances, it must be used in any quantitative interpretation or prediction of photoelectron spectra, since autoionizing Rydberg states may overlap and interact strongly (Mies 1968).

Mies gives a matrix equation (his equation (35)) for the transition amplitude vector in photoionization. Writing explicitly this expression for the amplitude to a channel α and assuming only a single Rydberg series, we obtain

$$t_\alpha^- = \sum_\beta z_{\alpha,\beta}\left\{t^{\mathrm{C}}F_{i,\beta} + \sum_{n^*} t^b_{n^*}V_{n^*}\sum_\nu \frac{F_{\nu,\beta}F_{\nu,i}}{(E-E_{\nu,n^*})}\right\}. \tag{8}$$

Here β is another index for the final continuum channel and $Z_{\alpha,\beta}$ is a normalization matrix element given in Mies's equation (66). The quantity $t^b_{n^*}$ is the electronic transition amplitude to the Rydberg state n^*, and V_{n^*} is the electronic part of the autoionization width, $\langle\psi^{\mathrm{el}}_{n^*}|H|\Psi^{\mathrm{el}}_f\rangle$. If we combine this equation with Mies (1968) equation (66) (using the index ν' in equation (66) to distinguish it from ν in equation (18)), and then employ relations which follow from the orthogonality of the matrix F,

$$\sum_\beta F_{\nu,\beta}F_{\beta,\nu'} = \delta_{\nu,\nu'}, \quad \sum_\beta F_{\nu,\beta}F_{\beta,i} = F_{\nu,i} \tag{9}$$

some algebra yields the following expression for the transition amplitude:

$$t_\alpha^- = \sum_\nu F_{\alpha,\nu}F_{\nu,i}C_\nu, \tag{10}$$

where

$$C_\nu = t^{\mathrm{C}}\left[1+q\sum_{n^*}\epsilon^{-1}_{\nu,n^*}\right]\Big/\left[1+i\sum_{n^*}\epsilon^{-1}_{\nu,n^*}\right]. \tag{11}$$

If the widths of the states are much less than the separation between successive states, autoionization will be important only if E is close to the energy of some state ν, n^*; then

$$C_\nu = t^{\mathrm{C}}(\epsilon_{\nu,n^*}+q)/(\epsilon_{\nu,n^*}+i),$$

which is Bardsley's result. If E is far from any sharp resonance, $C_\nu = t^{\mathrm{C}}$ for all ν, and

$$t_\alpha^- = t^{\mathrm{C}}\sum_\nu F_{\alpha,\nu}F_{\nu,i} = t^{\mathrm{C}}F_{i,\alpha},$$

which is the direct photoionization result. Suppose, however, that E falls precisely on a single resonance (ν', n^*) which does not overlap with any other resonance. Then

$$C_{\nu'} = t^{\mathrm{C}}q/i, \quad C_\nu = t^{\mathrm{C}} \quad \text{for} \quad \nu \neq \nu',$$

and

$$\begin{aligned} t_\alpha^- &= t^{\mathrm{C}}\left[\sum_{\nu\neq\nu'} F_{\alpha,\nu}F_{\nu,i} + F_{\alpha,\nu'}F_{\nu',i}\,q/i\right] \\ &= t^{\mathrm{C}}\left[F_{i,\alpha} - F_{i,\nu'}F_{\nu',\alpha}(1+iq)\right]. \end{aligned} \tag{12}$$

The first term in brackets is the contribution of direct photoionization and the second is the contribution of the autoionizing state. It is easy to visualize situations in which the latter is much larger than the former even if q is very small. Figure 1 shows such a case. Notice that if the second term predominates, the intensity ratio of two vibrational peaks $(\alpha+1, \alpha)$ in the photoelectron spectrum now has the form

$$\frac{\text{intensity }(\alpha+1)}{\text{intensity }(\alpha)} = \frac{F^2_{\alpha+1,\nu'}}{F^2_{\alpha,\nu'}}. \tag{13}$$

The intensity ratio is determined solely by Franck–Condon factors connecting the *autoionizing* state to the final state, in complete contrast to the direct photoionization result of equation (4).

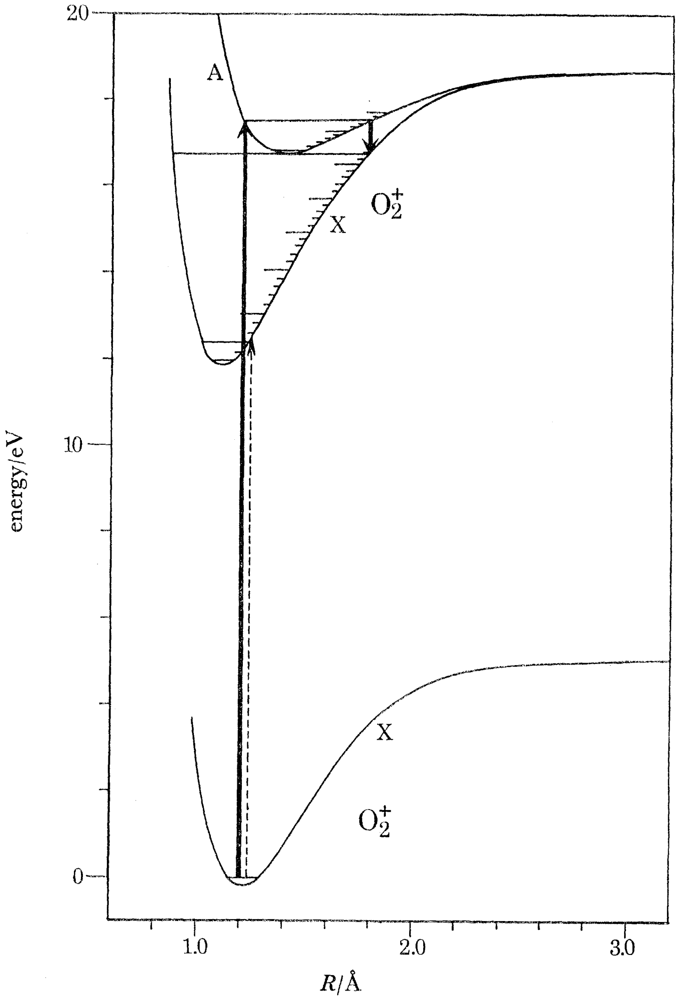

FIGURE 1. Production of high vibrational states of $O_2^+(X)$ by autoionization. Potential curves for the ground state $(X^3\Sigma_g^-)$ of O_2, the ground state $(X^2\Pi_g)$ of O_2^+, and a Rydberg state leading to $O_2^+(A^2\Pi_u)$ are taken from the curves of Gilmore. The direct photoionization (dashed line) predominantly populates vibrational state $\alpha = 2$ in $O_2^+(X)$, whereas the autoionizing transition (thick line) through vibrational state $\nu' = 8$ of the A state populates vibrational states in the vicinity of $\alpha = 27$, with weaker excitation of all lower states.

3. Calculations

The object is to provide a plausible but not quantitative explanation of O_2 photoelectron spectra when autoionization cannot be neglected. Using equation (12), the partial cross-sections for production of $O_2^+(X^2\Pi_g)$ in vibrational states $\alpha = 0$ to 14 have been calculated assuming that the excitation energy coincides with a Rydberg state leading to $O_2^+(A^2\Pi_u)$. The quantum number ν also runs from 0 to 14. Notice that equation (12) calls for Franck–Condon *amplitudes* F for the $O_2(X) \rightarrow O_2^+(X)$, $O_2(X) \rightarrow O_2^+(A)$, and $O_2^+(A) \rightarrow O_2^+(X)$ transitions, whereas only the Franck–Condon intensities F^2 have been calculated (the values of Nicholls (1965, 1968) have been used). The convention that all vibrational wavefunctions are real and positive at their left-hand classical turning points has been adopted. Since $F_{0,0}$ is always positive, the signs of the amplitudes in the 0–ν' progression are easily determined. Since the transition amplitude must change signs between two Condon loci in a vibrational progression, the remaining signs may be determined.

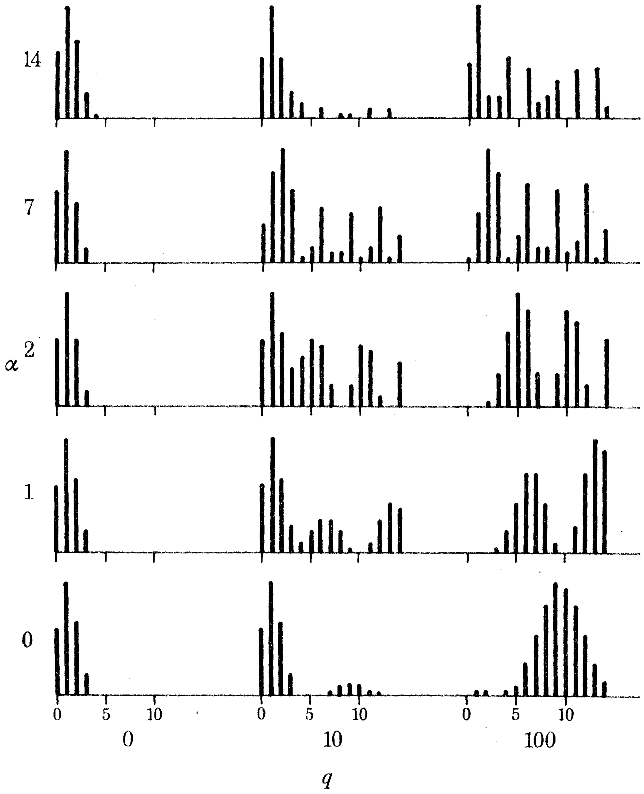

Figure 2. Calculated photoelectron spectra of O_2 in the presence of autoionization. The final state is $O_2^+(X)$, with vibrational quantum numbers $\alpha = 0$ to 14 shown on the abscissa. The intermediate, autoionizing state is any Rydberg state leading to $O_2^+(A)$, with vibrational quantum number as indicated on the ordinate. The spectra, all normalized to the most intense peak in the progression $0 \leqslant \alpha \leqslant 14$, are calculated for three values of the line profile index q. Peaks less than 5 % of the most intense peak are omitted.

The calculated relative partial cross-sections are shown in figure 2 for several vibrational states ν of the autoionizing state and for several values of q. An experimental value for q could be obtained from a high resolution photoionization spectrum in which an identified progression with a known Rydberg state has been completely resolved. The only conclusion one can safely draw from published O_2 absorption cross-sections (Huffman, Larrabee & Tanaka 1964) is that for Rydberg states leading to $A^2\Pi_u$ and $a^4\Pi_u$, q is much larger than 1 and probably larger than 10. More reliable values must await a more complete identification of the oxygen spectrum in this region.

The partial cross-sections for direct photoionization to the first five vibrational states of $O_2^+(X)$ are calculated to be in the ratio 0.60:1.00:0.67:0.24:0.05.

The first interesting result is in the series of spectra with $q = 0$. Physically, the limit of vanishing line profile index is approached when the transition probability to the ionization continuum f is very large compared to the transition probability to the autoionizing state. Even so, the photoelectron spectra are affected by the presence of the autoionizing state; the vibrational intensity distribution departs from the direct photoionization result (notice the change in relative intensities of $\alpha = 0$ and $\alpha = 2$ with increasing ν).

The limit of large q means that the final states f, α are much more likely to be populated through the autoionizing state than by direct photoionization, and the spectra for $q = 100$ approximate this limit. The calculated vibrational intensity distribution is almost completely determined by Franck–Condon amplitudes from the autoionizing state to the final state: for this reason the spectrum through $\nu = 0$ shows one broad maximum, centred at $\alpha = 9$. The spectra through higher vibrational states show intensity alterations identical to those one would observe in the corresponding v'' progression in the second negative system of $O_2^+(A \rightarrow X)$.

The series of spectra for $q = 10$ are the intermediate case, and show effects similar to those observed in the experiments. The vibrational peaks populated in direct photoionization are present, but with distorted relative intensities, and a large fraction of the ions produced have much vibrational excitation.

4. DISCUSSION

These calculations raise an interesting question: to what extent have photoelectron spectra previously reported been influenced by autoionization? As a general rule, one may say that if a molecule has an inner ionization potential less than 2 eV above the photon energy E being used, one will have Rydberg states of the molecule in the vicinity of E. If the geometry of the ionic state is rather different from that of the ground state of the neutral molecule, the Rydberg states will show extensive vibrational progressions. If there are no selection rules forbidding it, the Rydberg states will autoionize to photoionization continua at the same total energy at some rate Γ/h. If the oscillator strength to the Rydberg state is comparable to Γ times the differential oscillator strength to the ionization continuum of some lower ionic state, then the photoelectron spectrum associated with this lower state may show strong departures from the vibrational intensity distribution expected in direct photoionization.

In view of the large amount of data taken with helium resonance line excitation (21.21 eV), it becomes important to know orbital ionization energies in the 22 to 24 eV region, and to determine the geometry change upon removing electrons from such orbitals. One case which comes immediately to mind is the $2a_1$ orbital of methane, found by Hamrin, Johansson, Gelius, Fahlmann, Nordling & Siegbahn (1968) to lie at 23.1 eV. The width of the peak suggests that this orbital does affect the C–H bonding. It is conceivable that production of ground state CH_4^+ by 21.21 eV radiation proceeds through autoionizing Rydberg states, thus producing a photoelectron spectrum not representative of Franck–Condon ionization. This effect may explain some of the discrepancy between the values of the first vertical ionization potential of methane as determined from low-energy photoelectron spectra (Al-Joboury & Turner 1967) and from e.s.c.a. (Hamrin *et al.* 1968).

If helium resonance line excitation may show effects of autoionization, experiments with lower photon energies are even more suspect in this regard. For example, if the spectrum calculated in figure 2 for $v = 2$, $q = 10$ were observed under low resolution it might be misinterpreted as evidence for an additional low-lying electronic state of O_2^+. Indeed, Collin & Natalis (1968*b*) have claimed that the photoelectron spectrum of NO excited with neon resonance radiation shows a new 'state' of NO^+ appearing at about 14 eV, whereas Huber (1968) has given a different interpretation to the helium resonance line photoelectron spectra of Turner & May (1966), which show no structure at 14 eV. There are several excited states of NO^+ with large bond length arising from the $\pi^3\pi$ configuration in the 16 to 19 eV range. It is quite possible that the structure seen by Collin at 14 eV is a group of transitions to highly vibrationally excited NO^+ in its *ground* electronic state populated through autoionizing states leading to one of the excited ionic states. Higher states derived from the $\pi^3\pi$ configuration probably lie in the vicinity of the helium resonance line; thus the observed vibrational intensities in the 21.21 eV photoelectron spectrum may depart slightly from those of direct photoionization.

If autoionization is important at an energy E, a small change in this energy may drastically affect the vibrational intensity distributions in the photoelectron spectra. Such a moderate tuning could inadvertently be obtained if high source gas pressures produced asymmetric self-reversal of the rare gas resonance lines.

Note added in proof, (*May* 1970). Further comments on interpreting photoelectron spectra in the presence of autoionization are contained in an article entitled 'Effect of autoionization on the production rates of vibrationally excited O_2^+ by solar photoionization' (Smith 1970).

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