Vibrational Interference in the Decay of Core-Excited Nitric Oxide

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The nitrogen *KVV* Auger spectrum of nitric oxide contains peaks corresponding to the decay of neutral, core-excited NO to final states of NO^+. The position and shape of the peak resulting from decay to the ground state cannot be explained by the usual Franck-Condon analysis. Since the lifetime of the core-excited states is comparable to the characteristic vibrational time, it is necessary to include in the analysis the effects of interference between different vibrational states. When these are included, there is excellent agreement between the experimental and theoretical line shapes.

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In the analysis of spectral line shapes influenced by vibrational excitations or deexcitations it is necessary to perform a Franck-Condon analysis of all important transitions between the relevant potential surfaces. Implicit in this type of analysis, however, is the assumption that the levels involved are stationary states. If the lifetime of the electronic states is not long compared with the time for vibrational motion, this approximation is invalid and the vibrational levels are strongly mixed. In this case, the lifetimes of the states must be explicitly included in the line-shape analysis.

The effects of such lifetime-vibrational interference have been theoretically analyzed by Gel'mukhanov, Mazalov, and Kondratenko,[1] Kaspar, Domcke, and Cederbaum,[2] Correia *et al.*,[3] and Flores-Riveros *et al.*[4] and have been found to be important in the autoionization and Auger decay of core-excited molecules. Correia *et al.*[3] have discussed the autoionization and Auger spectra from carbon monoxide with both carbon and oxygen core excitation. They found conditions to be right for significant interference in the oxygen autoionization spectrum, but their experimental spectrum did not provide sufficient intensity to allow comparison. In the carbon spectrum the overall magnitude of the interference is predicted to be much smaller—probably too small to be observable. (We believe that there is an error in the calculated spectra presented by Correia *et al.* and that the interference effects can be observed in the oxygen spectrum.[5] These conclusions will be discussed elsewhere.[6])

We report here results for the autoionization decay of core-excited nitric oxide to the ground state of NO^+ that show for the first time pronounced interference effects even at resolution insufficient to resolve the vibrational structure. We find excellent agreement between our experimental data and theoretical spectra that include these interference effects. The calculations are made without any adjustable parameters except total intensity. Moreover, we find that the experimentally observed peak shape and position cannot be explained satisfactory unless these interference effects are taken into account.

Experimentally, we have measured the autoionization decay of nitric oxide core excited by 3400-eV electrons. The autoionization spectrum was obtained by measurement of electrons in coincidence with scattered electrons undergoing an energy loss of 400 eV, corresponding to the resonant excitation of a nitrogen 1*s* electron to the partially filled 2π orbital.[7,8] The experimental resolution in the energy-loss channel, 2 eV, is broad enough to assure population of the full envelope of allowed electronic and vibrational excitation.[7] A detailed description of the coincidence method and experimental apparatus is given by Haak *et al.*[9] The coincidence spectra in this case show only those events originating from the decay of neutral, core-excited nitric oxide (labeled N^*O), and thus represent the autoionization decay of this excited molecule. The autoionization populates the ground and excited states of the NO^+ ion. Figure 1 shows this spectrum. The highest kinetic energy peak (I) results from

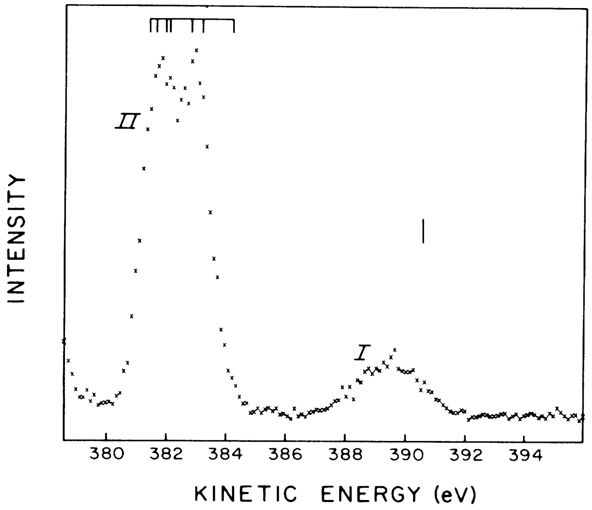

FIG. 1. High-kinetic-energy region of the nitrogen *KVV* Auger spectrum of nitric oxide. The vertical lines indicate the expected positions of the one-hole states of NO^+.

transitions to the ground state of NO^+ ($^1\Sigma^+$), and the next lowest group at 382 eV (II) from transitions to as many as eight excited states of NO^+.

The kinetic-energy scale was calibrated by measurement of the nitric oxide Auger spectrum simultaneously with the argon *LMM* and neon *KLL* Auger spectra.[10] The expected positions for the transitions to the states in NO^+ indicated in Fig. 1 were determined from the NO^+ ion energies reported by Edqvist *et al.*[11] and the N^*O energy measured by Tronc, King, and Read.[7] The overall uncertainties in the expected positions for these transitions are approximately ±0.1 eV.

Peak I is anomalously broad and displaced from the position calculated from the known energy of the ground state of NO^+ [see the dashed curve in Fig. 2(a)], indicating that vibrational structure in either the intermediate or final states, or both, may be important. Correct inclusion of vibrational broadening into the calculation of the spectrum depends on a consideration of the relative lifetimes for electronic deexcitation and vibrational motion. We first consider two extreme cases.

If the deexcitation is very fast compared to any vibrational motion, then the initial, intermediate, and final states of the process all have the same internuclear distance. In this case, the vibrational structure depends only on the properties of the initial and final states and not on the properties of the intermediate state. The vibrational structure can be calculated from the Franck-Condon factors for the direct transition from the ground state of NO to the ground state of NO^+. The calculated line shape based on this assumption is shown as the solid line in Fig. 2(a), where it is compared with the experimental data. We see that the calculated line shape fails to match the observed peak in either position or width.[12]

At the other extreme, we consider the case where the electronic deexcitation is very slow compared with the vibrational motion. In this case, the vibrational structure is calculated from the convolution of the Franck-Condon factors for the excitation of the intermediate state with those for its deexcitation to NO^+. Such a calculated spectrum (based on parameters for N^*O discussed below) is shown in Fig. 2(b). This spectrum is slightly broader than the experimental spectrum and does not match it in position. Thus, neither of these extreme assumptions is valid; it is necessary to consider the coupling of lifetime and vibrational motion.

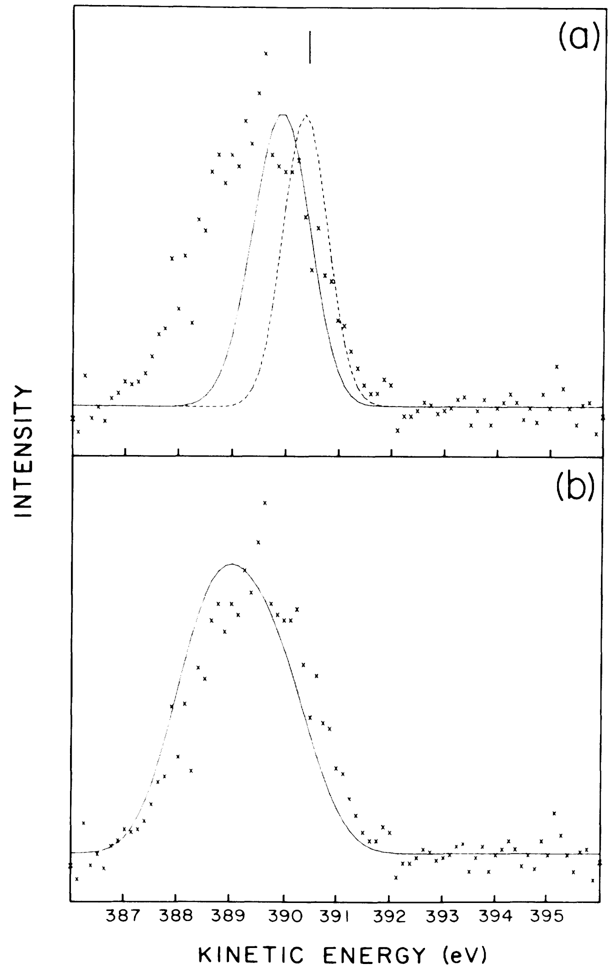

FIG. 2. (a) The NO^+ ($X,{}^1\Sigma^+$) peak. The points represent the experimental data. The dashed line is a single Gaussian of FWHM 1 eV positioned at the $v=0$ energy. The solid line is the expected line shape for a vertical transition $NO \rightarrow NO^+$. (b) The solid line is the expected line shape resulting from a convolution of Franck-Condon factors for the transition to the core-excited molecule with those to the ion, including the effect of an experimental resolution of 1 eV.

High-resolution electron-energy-loss measurements[7] on NO exhibit significant vibrational structure, and have been analyzed with the equivalent-cores assumption that core-excited N^*O is analogous to O_2. The lifetime width derived from the electron-energy-loss spectrum, 0.145 eV, is comparable to the vibrational spacing in the excited state, 0.19 eV, and therefore the deexcitation lifetime is comparable to the time for vibrational motion. These results are consistent with our failure to fit the data with calculations based on the assumption that one of these times is much shorter than the other.

Theoretical analysis[1-4] of lifetime-vibrational interference gives the following equation[3] for the intensity of an emission spectrum as a function of energy:

$$I(E)\propto\sum_f\left|\sum_n\frac{\langle f|n\rangle\langle n|0\rangle}{E-(E_n-E_f)+i\Gamma/2}\right|^2, \qquad (1)$$

which when expanded gives

$$\sum_f\sum_n\frac{(\langle f|n\rangle)^2(\langle n|0\rangle)^2}{[E-(E_n-E_f)]^2+\Gamma^2/4}+\sum_f\sum_{m\neq n}\frac{\langle f|n\rangle\langle n|0\rangle\langle f|m\rangle\langle m|0\rangle\{[E-(E_n-E_f)][E-(E_m-E_f)]+\Gamma^2/4\}}{\{[E-(E_n-E_f)][E-(E_m-E_f)]+\Gamma^2/4\}^2+(E_n-E_m)^2\Gamma^2/4}. \qquad (2)$$

Here 0 represents initial state, m and n intermediate states, and f the final state; E_f is the energy of the final state, E_n and E_m are energies of intermediate states, and Γ is the width for decay of the core-ionized state. The terms $\langle f|n\rangle$, etc., represent vibrational overlap integrals between the indicated states. In the limit that Γ is small compared with the difference $E_n - E_m$, this expression reduces to the first summation, which gives the convolution of Franck-Condon factors for the exciting transition with those for the deexcitation. This is referred to as the "direct" term. When Γ is large, then the entire expression reduces to Franck-Condon factors between the initial and final states and is independent of the intermediate state. This expression thus leads to the two extremes that have been discussed above. In the intermediate case, the various contributions must be calculated explicitly.

In order to perform this analysis we used values for vibrational constants for NO and NO^+ given in Huber and Herzberg,[13] and used the equivalent-core approximation for N^*O. With this approximation we assume that the vibrational constants are the same as for O_2, with appropriate adjustment for the difference in reduced mass. Our computations were performed with these values fixed; the only adjustable parameter was peak height.

The importance and magnitude of the interference effect can be seen in Fig. 3(a), which shows direct, interference, and total curves for excitation and deexcitation through one electronic state of N^*O (at infinite resolution and a lifetime width of 0.145 eV). The interference is strongly destructive on the low-energy side and constructive on the high-energy side of the peak. The interference results in a final profile that is substantially shifted to higher energy and slightly *narrowed* when compared to the direct profile. These results are in contrast to those reported by Correia *et al.*,[3] for CO, where the interference effects either are small or, even where large, are calculated by them not to have a major effect on either the position or shape of the peak.

Of the three terms, $^2\Sigma^+$, $^2\Sigma^-$, and $^2\Delta$, populated in the excitation to the π^2 configuration, selection rules for Auger decay allow decay to the $^1\Sigma^+$ ground state of NO^+ only from the $^2\Sigma^+$ and $^2\Delta$ terms of N^*O. Thus, we expect the final spectrum to be the sum of two individual spectra. Using values from Ref. 7 for the $^2\Sigma^+$-$^2\Delta$ term splitting, for the relative populations of these two states, and for the lifetime of the core-hole state, we have computed the expected spectrum. We have also assumed that the two electronic states decay to the ground state of the ion with equal probability. The calculated spectrum is shown in Fig. 3(b) for the case of no instrumental contribution to the linewidths.

Finally, Fig. 3(c) shows the curve computed with a spectrometer resolution of 1 eV. It is evident that the computed curve fits the data very well. Inclusion of interference yields a curve between the extremes of short and long lifetimes shown in Fig. 2. The net effects are a shift in peak position to higher energy and a slight de-

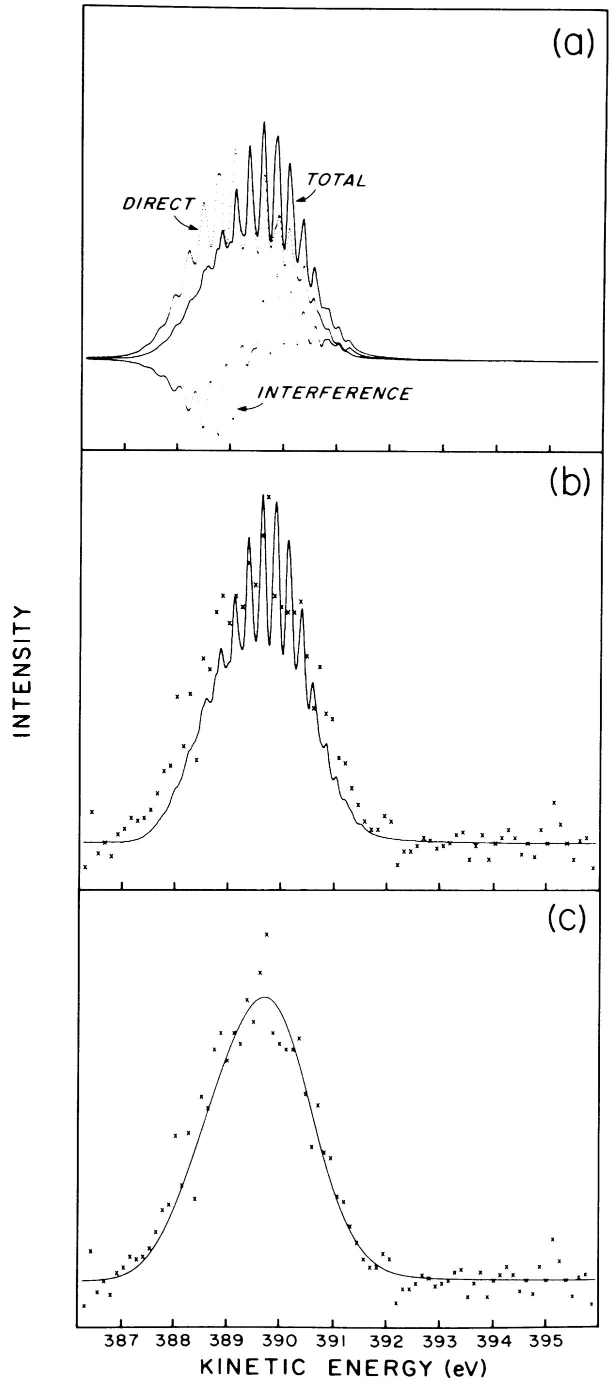

FIG. 3. (a) Direct, interference, and total curves for excitation and deexcitation through one excited state of N^*O at infinite resolution. (b) Expected line shape including two states of N^*O at infinite resolution. (c) Total curve computed with a spectrometer resolution of 1 eV. (b) and (c) are superimposed on the data as in Fig. 2.

crease in FWHM.

We have computed interference line shapes for other peaks in the nitrogen and oxygen spectra of NO and of O_2. The results are all consistent with our measurements.[14] We find that every peak in a spectrum must be carefully analyzed for interference effects. The nature of the effects is a sensitive function of initial-, intermediate-, and final-state bond lengths and vibrational parameters. While it is difficult to generalize about situations in which interference will play a major role in determining peak shape, there are certain criteria that must be satisfied. There must be significant population of more than one vibrational level in the core-excited molecule. Otherwise, the summation in Eq. (1) reduces to the direct term only. The lifetime width of the core-excited state must be comparable to the spacings between vibrational levels. The lifetime widths of C, N, O, and F satisfy this criterion, and all may exhibit interference, especially N, O, and F. Effects are especially prominent if the molecule undergoes a large change in equilibrium bond length in the transition, core-excited → final-state ion. When this occurs the deexcitation vibrational manifold is quite complex and undergoes significant modification. We conclude that both vibrational structure (in core-excited and final-state ion) and lifetime-vibrational interference in the core-excited molecule must be taken into account to correctly explain and interpret autoionization spectra.

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