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Molecular effects on inner-shell lifetimes: Possible test of the one-center model of Auger decay

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Experimental 1*s* linewidths for compounds containing carbon, nitrogen, and oxygen are much greater than those predicted for the free atoms. Using a one-center model, we have determined the effect of molecular composition on the linewidth. The predicted linewidth in methane is 1.7 times that for a carbon atom. Increasing the electronegativity of ligands decreases the predicted linewidth; this result is in contrast to the predictions of the multicenter model [E. Hartmann, J. Phys. B **21**, 1173 (1988)]. Except for CO_2, the theoretical linewidths are in good agreement with experiment.

Core-ionization energies are known to reflect such molecular properties as charge distribution and the ability of a molecule to accept charge at a particular site. Less understood is the influence of molecular composition on the lifetime of a core hole, although the possibility that there are chemical effects on the deexcitation lifetimes of molecules with inner-shell vacancies has been explored over a period of years.[1-5] Evidence for chemical effects on deexcitation rates in simple molecules has been advanced,[1] but the case for such effects has not been made convincingly.[6] However, an increasing body of experimental results[4,6-11] from high-resolution inner-shell spectroscopy as well as from theoretical calculations[12,13] indicates that the lifetimes of 1*s* holes in molecules may be significantly different from those predicted for free atoms and may depend on molecular composition.

A variety of experiments involving photoelectron spectroscopy,[6] energy-loss spectroscopy,[7-11] and photoabsorption spectroscopy[4] provides information on the lifetime of 1*s* holes in small molecules. Traditionally, these lifetimes have been compared with theoretically predicted lifetimes for the free atom[14,15] and the agreement has not been very good. Examples are found in Table I, where it can be seen that the experimental 1*s* linewidths

TABLE I. Theoretical and experimental 1*s* linewidths (meV).

Element	Compound	Theoretical[a] This work	Theoretical[a] Ref. 12	Experimental	Valence-e^- density
Carbon	C	56[b]	53		4
	CO_2	66		148[c]	4.2
	CO	73		85[d]	4.4
	CH_4	96	75	94[c]	5.0
	CH_3F	88			4.8
	CH_2F_2	79			4.6
	CHF_3	71			4.3
	CF_4	63	88		4.1
	C_2H_2	96	92		
	C_2H_4	95	89	110[e]	5.1
	C_2H_6	94	85		5.0
Nitrogen	N	88[b]			5
	N_2	120		123[f]	5.6
	NO	138		143[g]	6.0
Oxygen	O	131[b]			6
	O_2	169		180[h]	6.7
Neon	Ne	245[b]		230[i]	8

[a] Calculated from the Auger transition rate, τ^{-1}. Linewidth is $\hbar/\tau$.
[b] Reference 15.
[c] Reference 10.
[d] Reference 8.
[e] Reference 4.
[f] Reference 11.
[g] Reference 9.
[h] Reference 7.
[i] Reference 6.

(inverse lifetimes) for carbon, nitrogen, and oxygen atoms in molecules are as much as twice the linewidths predicted theoretically for the corresponding free atoms. In addition, different compounds containing the same core-excited element give different values. Only for neon is there good agreement between experiment and theory; this is the only system for which the calculations and the measurements have both been done for a free atom.

It is by no means certain that these experimental values represent the true linewidths. In some cases, there is probably unresolved vibrational structure contributing to the reported linewidth.[10] Shaw and co-workers[8] have noted that the linewidth is "the parameter that is most sensitive to apparatus sensitivity" because of the existence of voltage drifts in the apparatus. Nevertheless, it has been suggested that these experimental linewidths may be evidence for "a dependence of the lifetime on the chemical environment."[4] There have been other suggestions of such chemical effects.[1–3,5,12,13] It is, therefore, of interest to investigate the magnitude of possible molecular effects on inner-shell lifetimes.

For light elements, the inner-shell lifetime is determined almost entirely by the Auger rate. Fluorescence yields range from 0.0024 for carbon to 0.0164 for neon,[15] and, therefore, the effect of x-ray emission on the transition rate can be ignored. The Auger rate for these systems depends on the square of the Coulomb matrix element

$$\langle \psi_{1s}\chi | 1/r_{12} | \psi_v \psi_{v'} \rangle ,$$

where ψ_{1s} represents the wave function for the 1*s* electron, χ is the continuum electron, and ψ_v and $\psi_{v'}$ are the wave functions for the valence electrons that participate in the Auger process. Because the 1*s* electron is strongly localized on a specific atom, only that part of the valence wave function that is close to this atom contributes to the matrix element. The Auger rate should therefore be affected by chemical bonding that influences this local density.[1–3,6] Furthermore, in calculating the total Auger rate it is necessary to sum over all possible final states. It is this sum (rather than changes in the matrix elements) that leads to the factor of 4 increase in linewidth as we go from carbon to neon. This effect must also be taken into account when we consider the differences between atoms and molecules.

An essential difference between atoms and molecules is that the atom has some of its valence orbitals filled and some completely empty, whereas in the molecule all of the same set of atomic orbitals are occupied, but only partially. The effect of this difference can be illustrated by a comparison between a carbon atom and a methane molecule. For simplicity, we consider only the *p* electrons and assume that the bonding in methane is purely covalent.

Carbon atom has a *p*-shell configuration that is p^2. According to McGuire,[14] the transition rate is reduced from that for a p^6 configuration by a factor of 15. This reduction arises from the sum over final states—for p^2 there is only one final state, whereas for p^6 there are 15. In methane, on the other hand, the same two *p* electrons are distributed over all six *p* orbitals, so that the configuration might be represented as $(p^{1/3})^6$. According to the one-center model[16] for molecular Auger transitions, the rate should be reduced from the closed-shell rate by $(\frac{1}{3})^2$. Thus on this basis we expect the rate in methane to be faster than that in carbon atom by the ratio of $\frac{15}{9}$. (If we include the role of the *s* electrons, and assume that the matrix elements leading to *ss*, *sp*, and *pp* final states are the same, the ratio of rates decreases to $\frac{7}{6}$).

The foregoing analysis ignores the polarization of the valence electrons caused by the presence of the core hole. For a carbon atom the configuration is still p^2. For methane, however, as much as one electron may be withdrawn from the surrounding hydrogens to screen the core hole. The appropriate configuration might then be $(p^{1/2})^6$. The corresponding rate would be $\frac{1}{4}$ of the closed-shell rate and the ratio of molecular-to-atomic rates would be $\frac{15}{4}$. (Including *s* electrons and taking the configuration to be $s^2(p^{1/2})^6$, the rate of methane is predicted to be faster than the rate in carbon atom by a factor of 1.8.)

Additional polarization effects can result if the hydrogens are replaced by electronegative ligands. In carbon tetrafluoride, there is decreased electron density at the carbon relative to that in methane, and there should be a slower transition rate in carbon tetrafluoride relative to methane. Such an effect might account for the differences between carbon monoxide and ethylene seen in Table I.

The experimental linewidths for molecules given in Table I are not for normal Auger transitions from core-ionized species but for autoionizing transitions from neutral core-excited species. Thus the number of valence electrons is greater than would be the case for normal Auger emission. This factor may influence the rate of the deexcitation process.

The foregoing discussion provides arguments that the lifetimes for molecular Auger transitions may be significantly shorter than those for atomic transitions and that there may be a marked influence of the molecular composition on the lifetime. Calculations by Hartmann[12] support this conclusion. We have also investigated these possibilities with quantitative theoretical calculations. Although we, like Hartmann, find that there are chemical effects on lifetime, our predictions are distinctly different from his.

The calculation of Auger transition rates presents a formidable problem because often the two-hole final states cannot be accurately described in an independent-particle model and, for molecules, because of the difficulty of representing continuum wave functions in a multicenter framework. In general, the problem has been simplified by using atomic radial matrix elements together with the one-center approximation.[16] In this, it is assumed that there are no *interatomic* transitions in the molecule,[17] but that all of the transition moment arises from atomic wave functions that are centered on the atom with the core hole. A computer code using this approximation together with complete neglect of differential overlap (CNDO) or intermediate neglect of differential overlap (INDO) molecular wave functions to predict Auger spectra has been written by Larkins and Tulea[18] and gives results in reasonable agreement with experiment. Using this program with experimental geometries, the INDO approximation, the equivalent-core approximation to give the effect of the core hole on the valence electrons, and atomic radial matrix elements from Walters and Bhalla,[15] we have obtained the absolute transition rates for the molecules listed in Table I. In the last column of the table we give the Mulliken populations for the valence electrons of the core-ionized atom.

For comparison, the results obtained by Hartmann[12] are also presented in Table I. The one-center approximation that we have used is in contrast to the approach used by Hartmann, who used multicenter wave functions. Disagreement between the two sets of results may be due to this difference.

From the theoretical results in Table I, we note several trends. As predicted, there is a striking increase of the theoretical linewidth for methane relative to that for carbon atom. The ratio of the linewidths is 1.72, in agreement with the estimate mentioned earlier (but different from the ratio of 1.4 found by Hartmann). Most of this increase is due to the polarization of the valence electrons by the core hole. If valence wave functions for methane in the ground state are used, this ratio is only 1.07.

In agreement with our expectations, we observe a decrease in the linewidth as the methyl hydrogens are replaced by electronegative ligands. This is especially evident in the fluoromethane series where each replacement of hydrogen by fluorine results in a decrease in the valence-electron population of about 0.2 with a concomitant decrease of 8–9 meV in linewidth. Also, a notable decrease in the theoretically predicted linewidth is seen in the CH_4, CO, CO_2 series. The *decrease* in linewidth from 96 to 63 meV as we go from CH_4 to CF_4 is in striking contrast with the results obtained by Hartmann, who found an *increase* from 75 to 88 meV. We see then that the prediction based on the multicenter model is the reverse of the prediction based on the traditional one-center model. In CF_4, the high electron density on the fluorines may contribute significantly to the Auger transition rate, even though such interatomic transitions are not expected.[17] Thus, experimental measurement of linewidths may provide an important test of the one-center model.

For the C_2H_n series, neither the valence population nor the predicted linewidth depend significantly on the degree of saturation of the carbon–carbon bond. Hartmann's results for these molecules are in agreement with ours.

The agreement between experiment and our theoretical results is generally good. The most valid comparison is for NO where both calculation and experiment refer to deexcitation of the neutral core-excited species. The calculation for the C_2H_n series is also for the neutral core-excited molecule, but the lifetime was obtained by interpolation of the lifetimes of the core-ionized states resulting from the neutral ground state and a dianion ground state. The agreement of the experimental and theoretical linewidths for ethylene is not as good as it is for NO.

Except for CO_2, the agreement is good for the remaining molecules. However, the calculated values are for deexcitation of the core-ionized molecule, while experimental values are for deexcitation of the core-excited neutral molecule. In addition, for O_2 the linewidth is calculated for the deexcitation of core-ionized singlet oxygen. These approximations are necessary because the CNDO-INDO program does not handle an open shell in the initial state.

Carbon dioxide is the only molecule thus far that shows poor agreement between experiment and our calculations. From the data given by Tronc, King, and Read[10] it appears that the reported experimental linewidth of 148 meV refers to deexcitation from a state in which a core electron has been excited to a Rydberg orbital rather than one in which a core electron has been excited to the lowest unfilled molecular orbital. The latter core-excited state has the same valence configuration as NO_2 and is probably bent in its most stable state.[19] The peak corresponding to the excitation of this state is about 600 meV wide, presumably because of unresolved transitions to bending and stretching levels.[10] For core ionization to CO_2, the excited state is, however, linear and only symmetric stretching modes should be excited. For a transition of a core electron to a Rydberg orbital, the configuration should be between these extremes, so that the linewidth might be broadened by unresolved vibrational structure. On the other hand, the fact that the reported experimental linewidth for CO_2 is greater than for CH_4 and also greater than that predicted by our calculations, may be evidence for a failure of the one-center model. Arguing against this possibility is the linewidth for CO, which is narrower than that of CH_4, in keeping with the predictions of the one-center model.

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