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On the photoelectron spectrum of *p*-benzoquinone

John F. Stanton[a)] and Kurt W. Sattelmeyer[b)]
Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry,
The University of Texas at Austin, Austin, Texas 78712

Jürgen Gauss
Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Michael Allan, Tomas Skalicky, and Thomas Bally
Institute for Physical Chemistry, University of Fribourg, Perolles, CH-17 Fribourg, Switzerland

A high-resolution photoelectron spectrum of *p*-benzoquinone in the low energy (9.5–11.5 eV) region is reported and analyzed with the aid of simulations based on high-level *ab initio* calculations. The results generally support the notion that the two prominent spectral features in this region are each due to a pair of final ion states. The lower energy feature beginning near 10 eV is due to oxygen lone-pair ionizations, while that beginning near 11 eV comes from π electron removal. Contrary to previous interpretations of the spectrum, however, the results of this study indicate that the two π states are nearly degenerate, with the strongest peak in the photoelectron spectrum representing a convolution of the corresponding pair of 0–0 ionizations.   © *2001 American Institute of Physics.* [DOI: 10.1063/1.1381575]

The low-energy region of the photoelectron spectrum of *p*-benzoquinone (PBQ) exhibits two gross features; each of these possesses considerable vibrational structure, and the assignment of this region of the spectrum has been a matter of much controversy in the past.[1] Koopmans' theorem predicts that the four lowest-lying cation states are *g* and *u* combinations of lone-pair (*n*) and π ionizations, and just about any sequence of these states has been postulated to explain the photoelectron spectrum. It is generally believed that the two main features each correspond to a pair of final states. Perhaps the most detailed and convincing work done to interpret the spectrum was that of Dougherty and McGlynn,[2] who studied substituted PBQs with high-resolution photo-electron spectroscopy and used chemical intuition to infer that the lower feature (which starts at about 10 eV) is due to the n_- (b_{3g} symmetry) and n_+ (b_{2u} symmetry) states while that beginning near 11 eV is due to the π_+ (b_{3u}) and π_- (b_{1g}) states.[3] Within the molecular orbital approximation, the ionization events can be thought of as ejections of electrons from the orbitals shown in Fig. 1. This qualitative picture is now generally accepted, as is the belief that the n_- state lies beneath n_+. However, the magnitude of the splitting between n_- and n_+ states as well as the ordering of the π_+ and π_- states has not been firmly established.

Previous calculations have been inadequate to resolve almost all of the questions regarding the 9.5–11.5 eV photoelectron spectrum of PBQ. Perhaps the best work to date is that of Braga and Larsson,[4] who carried out complete-active-space self-consistent-field (CASSCF) calculations, albeit with a limited (double-zeta) basis set. In that work, a through-bond interaction model was used to rationalize certain features of the spectrum, and they indeed found that the n_- is the lower lone-pair state with a calculated splitting of 0.15–0.20 eV. For the two low-lying π states, the calculations of Ref. 4 found the π_+ to lie lower; calculated splittings ranged from 0.08 to 0.31 eV. Significantly, inclusion of dynamic correlation *via* configuration interaction significantly lowered the gap between the two π states. Experimentally, the splitting appears to be about 0.2 eV with features at 10.93 and ~11.1 eV representing the respective origins.

A detailed analysis of the 9.5–11.5 eV photoelectron spectrum of PBQ is the subject of this communication. To this end, we have recorded a new high resolution spectrum and carried out simulations that are parametrized by high-level *ab initio* calculations. Simulations were carried out with the linear vibronic coupling (LVC) model of Cederbaum and co-workers,[5] which requires the following input parameters: Vertical ionization energies, harmonic vibrational frequencies of the neutral, gradients of the cation states at the neutral geometry, and nonadiabatic coupling strengths between interacting cation states. All of these were obtained using coupled-cluster theory.[6] The geometry and harmonic force field of the neutral were calculated with the coupled-cluster singles and doubles (CCSD)[7] method and a triple-zeta plus double polarization (TZ2P) basis set[8] using analytic first[9] and second[10] derivative techniques.[11] Gradients of the cation states were calculated analytically[12] with the equation-of-motion (equivalent to linear response) CCSD method for ionized states[13] (EOMIP-CCSD) and the same basis. More sophisticated calculations were carried out to estimate the

[a)]Electronic mail: stanton@jfs1.cm.utexas.edu
[b)]Present address: Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602.
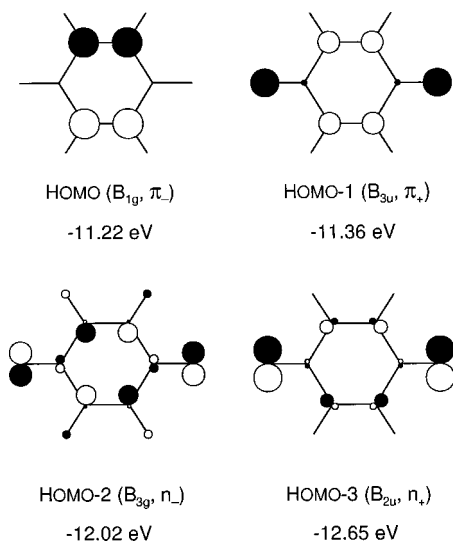
FIG. 1. The four highest-lying occupied molecular orbitals of *p*-benzoquinone. The orbital energies are those obtained with the TZ2P basis at the geometry specified in Ref. 11. The deficiencies of Koopmans' approximation for the present problem can clearly be seen in comparing these results with the true order of ion states (see Table I).

four relevant vertical ionization potentials of PBQ. First, EOMIP-CCSD calculations were performed with two large atomic natural orbital (ANO) basis sets, both based on those developed by Roos and co-workers.[14] In the first (ANO1), the nonhydrogen atoms are described by a $4s3p2d1f$ basis and the hydrogens by $3s2p1d$; the second set (ANO2) includes one additional contracted function of each type ($5s4p3d2f$ on C and O; $4s3p2d$ on H). Second, the effects of triple excitations on the ionization potentials were assessed by performing linear response CC calculations using the CC3 approximation,[15] as described in Ref. 16. A standard double-zeta plus polarization (DZP) basis[17] was used in the latter calculations, and core correlation effects were not considered. All calculations in this work used spherical har-

monic representations of d and f polarization functions and a local version of the ACES II program system.[18]

Vertical ionization potentials (in eV) for the n_-, n_+, π_+, and π_- states, respectively, with the DZP, TZ2P, ANO1, and ANO2 basis sets are: 9.85, 10.13, 10.89, and 11.08 (DZP); 10.09, 10.39, 11.11, and 11.21 (TZ2P); 10.22, 10.53, 11.20, and 11.28 (ANO1); 10.29, 10.60, 11.26, and 11.29 (ANO2). Values obtained at the CC3 level with the DZP basis are 9.60, 9.85, 10.77, and 10.82. Assuming additivity of triple excitation and basis set effects provides the following set of "best theoretical estimate" vertical ionization energies

$$10.05 \pm 0.10 \ (n_-), \quad 10.30 \pm 0.10 \ (n_+),$$

$$11.15 \pm 0.10 \ (\pi_+), \quad 11.05 \pm 0.20 \ (\pi_-),$$

where it should be noted that the ordering of the π states differs from both that deduced by Dougherty and McGlynn and that found at the CCSD level. This is due to a large triple excitation contribution to the π_- vertical ionization energy, which also serves as the reason for the more conservative uncertainty assigned to this quantity.

A brief discussion of the spectrum based on the calculations presented thus far is warranted at this point. The results appear to be largely in qualitative agreement with previous interpretations and also in quantitative agreement with the spectrum recorded in the course of this work, where the most prominent features are found at 10.00, 10.25, 10.94, and 11.12 eV. If one adopts the spectroscopic interpretation of Dougherty and McGlynn,[2] these correspond to the n_-, n_+, π_+, and π_- ionizations, respectively. Comparison with the theoretical estimates above shows essentially perfect agreement for the lower two ionizations, and it is tempting to attribute the disagreement in the π state values to a misassignment in Ref. 2. If the assignment is reversed, i.e.,
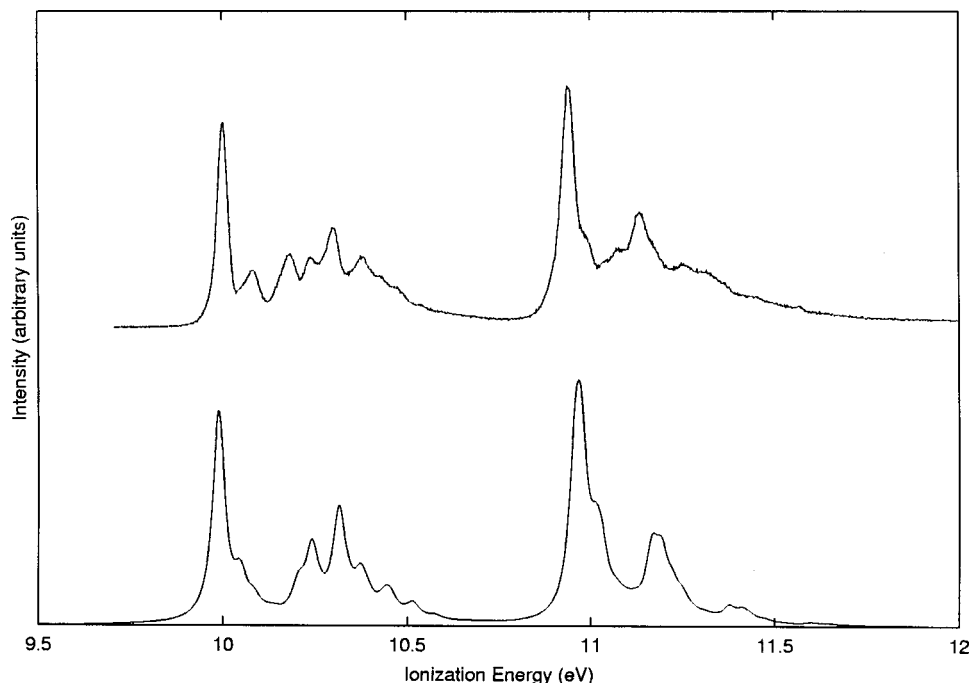

FIG. 2. Experimental (upper trace) and simulated (lower trace) photoelectron spectra of *p*-benzoquinone over the 9.5 to 11.5 eV energy range.

TABLE I. Vertical ionization potentials, vibrational energy level spacings (ω) and gradients (κ) for totally symmetric vibrations of *p*-benzoquinone cation states, and vibronic coupling strength (λ). All quantities are given in electron volts, with gradients and vibronic coupling strength expressed in the normal coordinate representation of the neutral. $\omega(n_-,n_+)$ is the frequencies of the vibronic coupling mode in the diabatic basis.

		Vertical ionization potentials			
		n_-	n_+	π_-	π_+
		10.05	10.33	11.08	11.08
		Totally symmetric frequencies and gradients			
Mode	ω_i	$\kappa_i^{n_-}$	$\kappa_i^{n_+}$	$\kappa_i^{\pi_-}$	$\kappa_i^{\pi_+}$
1	0.05600	0.02591	0.06664	0.04437	-0.04890
2	0.09539	-0.03719	0.00232	-0.01422	-0.02160
3	0.14687	-0.01394	-0.02633	0.04115	0.04225
4	0.20962	0.02593	-0.06246	-0.07015	-0.19772
5	0.22077	-0.12291	0.08668	0.17581	0.002941
		Vibronic coupling constants			
		ω_{n_-,n_+}	ω_{π_-,π_+}		
		0.093	$\cdots$		
		λ_{n_-,n_+}	λ_{π_-,π_+}		
		0.10	$\cdots$		

IP(π_-) below IP(π_+), then the discrepancies are reduced to 0.03 and 0.11 eV, both of which fall within the estimated uncertainties of the calculated values.

While highly accurate calculations of vertical ionization potentials are often useful and indeed apparently helpful in analyzing the currently accepted assignment of PBQ, it would clearly be better to extend the theoretical treatment to include the vibrational structure seen in the spectrum. It is possible that ionization potentials might agree satisfactorily with a given assignment of ionic states while the vibrational structure (if calculated) would be incompatible with the same assignment. This second dimension in the theoretical analysis of electronic spectra has long been advocated by Cederbaum and co-workers,[19] who have emphasized the important role that vibronic coupling plays in final ionic states where

quasidegeneracies are ubiquitous. The LVC model has recently been implemented by two of us (J.F.S. and K.W.S.), and is used here to simulate the 9.5–11.5 eV potential energy surface (PES) of PBQ. The parameters used in the simulation shown in Fig. 2 are based on *ab initio* calculations[20] and documented in Table I.

The relatively good qualitative agreement between theoretical and experimental spectra leaves little doubt that the assignment of Ref. 2 is correct for the lower cationic states. However, the standard interpretation of the higher energy part of the spectrum is that the peaks near 10.9 and 11.1 are the origins of the π_+ and π_- ionizations, respectively. Simulations carried out with gaps of ~0.1 eV (as suggested by the best *ab initio* estimates of the vertical ionization energies) were unable to satisfactorily reproduce this region of
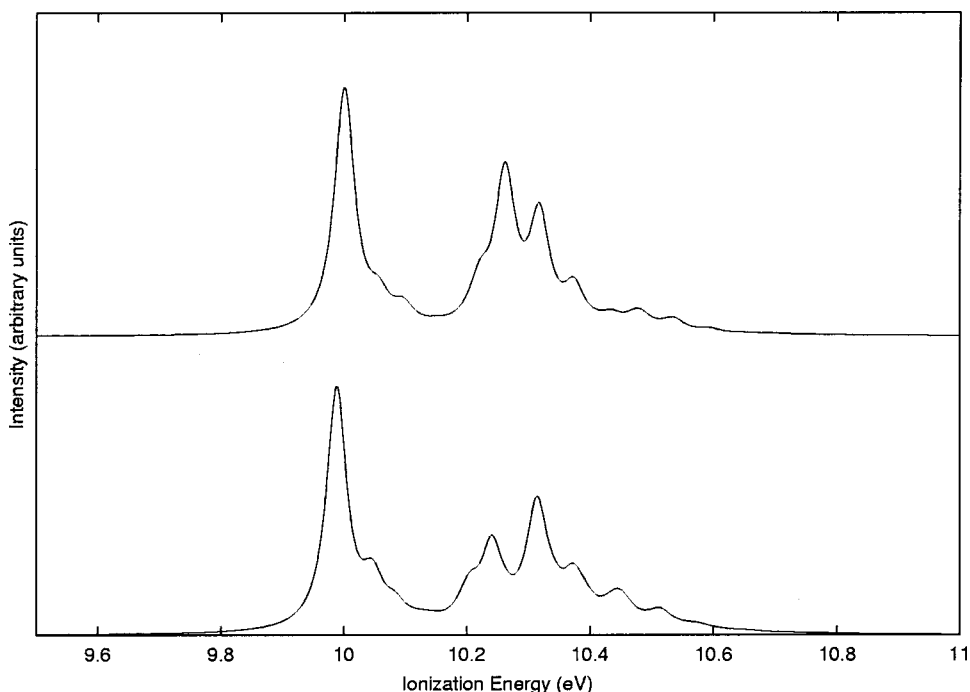

FIG. 3. Simulated photoelectron spectrum for the first two (n_+ and n_-) ionization events. Lower trace includes vibronic coupling, while λ is set to zero in the upper trace.

the spectrum. The principal problem is that there are rather large gradients on the two π state surfaces for the two totally symmetric stretching modes of the benzene ring (modes 4 and 5, see Table I). Hence, vibrational structure should be seen in both states with relatively strong features offset by approximately $+0.2$ eV with respect to the origins. If the gap between the two states is indeed of magnitude 0.1 eV or greater, one would therefore expect to see four strong peaks in the spectrum while only two are observed. However, by lowering the gap used in the simulations, satisfactory agreement with experiment is achieved. It is noteworthy that the relative strengths of the lowest energy features in the n and π regions of the spectrum are beautifully reproduced in the simulation, which serves as a consistency check on our interpretation that the bands centered near 11.0 and 11.2 eV are convolutions of features that correspond to *both* π_- and π_+ ionizations.

Based on the work presented in this communication, it is our belief that the 9.5–11.5 eV photoelectron spectrum of PBQ is now completely understood. The perceptive interpretation of the spectrum deduced by Dougherty and McGlynn using chemical substitution methods appears to be largely correct. The only minor modification of their interpretation centers on the higher energy region of the spectrum, where it appears that the π_- and π_+ states are nearly degenerate.

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