

# Electron-impact spectroscopy of various diketone compounds<sup>a)</sup>

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The spectra of the diketone compounds biacetyl, acetylacetone, acetylacetone, 1,2-cyclohexanedione, and 1,4-cyclohexanedione have been investigated by the technique of low-energy variable-angle electron energy-loss spectroscopy. With this method low-lying, spin-forbidden transitions have been observed. The energy difference between the lowest spin-allowed and spin-forbidden  $n \rightarrow \pi^*$  excitations in the acyclic diketones is found to be 0.35 eV, on average, which is nearly the same as that of comparable acyclic monoketone compounds; in 1,2-cyclohexanedione, however, this energy difference is 0.84 eV, more than twice as large. This discrepancy in the magnitude of the  $n \rightarrow \pi^*$  singlet-triplet splittings may be attributed to differing amounts of overlap between the initial and final orbitals.

## I. INTRODUCTION

Due to their importance in photochemistry and photo-physics, diketones have been studied extensively by both spectroscopic<sup>1-5</sup> and theoretical<sup>6-9</sup> methods. Compounds with two carbonyl groups provide useful structures for the study of intramolecular energy transfer, found to be a relevant process in both singlet and triplet excited states<sup>10</sup> and interactions involving remote carbonyl groups.<sup>11</sup> Work has been performed, primarily photoelectron spectroscopy,<sup>12</sup> in order to identify the mechanism by which carbonyl groups interact with each other. Even though the "through-space" interaction is expected to be small between two carbonyl groups in the same molecule,<sup>8,13</sup> the "through-bond" interaction leads to molecular orbitals with clearly split energies.<sup>14</sup>

In order to more fully understand the nature of the interaction between the carbonyl groups in diketone compounds it is helpful to have a complete picture of the low-lying electronic states, both allowed and forbidden. With the exception of biacetyl, the low-lying triplet states have not been definitively detected in most larger diketones. In biacetyl the two lowest singlet-triplet transitions have been observed in fluorescence<sup>2</sup> and by optoacoustic spectroscopy.<sup>1</sup> Electron-impact spectroscopy is a useful technique for observing and identifying forbidden, especially spin-forbidden, transitions in spectra. It is known that a spin-forbidden band exhibits a relatively constant intensity with scattering angle while a spin-allowed band is strongly forward peaked, falling by two orders of magnitude between the scattering angles  $10^\circ$  to  $90^\circ$ .<sup>15</sup> The combination of these effects results in a relative intensity increase of a spin-forbidden band with increased scattering angle. Another advantage of the electron-impact method is that spectral features in the far ultraviolet are easi-

ly examined. The compounds biacetyl, acetylacetone, acetylacetone, 1,2-cyclohexanedione, and 1,4-cyclohexanedione were chosen for study as representative samples of such compounds.

## II. EXPERIMENTAL

The electron spectrometer and the methods of data accumulation and analysis have been described previously.<sup>16</sup> Briefly, an electron beam is energy selected by a hemispherical electrostatic energy analyzer (and the associated focusing lenses) and scattered from the target vapor in a collision cell. In this work the incident beam current was between 0.5–10 nA and was typically 3 nA. Sample pressures were estimated to be between 1–10 mTorr. Electron energy losses were determined at angles between  $0^\circ$ – $90^\circ$  by means of a second electrostatic energy analyzer and detector.

The spectrometer resolution (as measured by the full width at half-maximum of the elastically scattered feature) varied between 50 and 125 meV for all reported spectra and was typically 85 meV. Peak locations determined from the spectra have an estimated uncertainty of  $\pm 0.07$  eV and Franck-Condon limits are estimated to be within  $\pm 0.15$  eV.

Liquid samples of biacetyl (Matheson, Coleman, and Bell 97 + %), acetylacetone (J. T. Baker 99.7%), acetylacetone (Aldrich 97%), and 1,2-cyclohexanedione (Aldrich 98%) were subjected to three freeze-pump-thaw cycles and used without further purification. 1,4-Cyclohexanedione (Aldrich 98%), a room temperature solid, was warmed to approximately  $50^\circ\text{C}$  during scanning to provide sufficient vapor pressure.

## III. RESULTS

### A. Biacetyl (2,3-butanedione)

The biacetyl molecule is of  $C_{2h}$  symmetry with the two highest occupied molecular orbitals being largely nonbonding and confined to the oxygen atoms. The degeneracy of the two oxygen nonbonding orbitals  $n_1$  and  $n_2$  is lifted by the interaction of these two orbitals. The levels arising from the symmetry-adapted linear combinations of these orbitals are

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designated  $n_+$  and  $n_-$ , where  $n_{\pm} = 1/\sqrt{2}(n_1 \pm n_2)$ , with symmetries  $a_g$  and  $b_u$ , respectively. The energy difference is 1.9 eV, with IP( $n_+, a_g$ ) = 9.55 eV and IP( $n_-, b_u$ ) = 11.45 eV.<sup>17</sup> For two carbonyl groups bonded directly together the difference in energy between the  $n_+$  and  $n_-$  orbitals is found to be relatively independent of torsional angle,<sup>17</sup> implying that the through-bond interaction dominates over the through-space interaction even for biacetyl. The next two lower occupied  $\pi$  orbitals have ionization potentials: IP( $b_g$ ) = 13.20 eV and IP( $a_u$ ) = 14.73 eV.<sup>18</sup> The two lowest unoccupied molecular orbitals have a  $\pi^*$  nature with  $\pi^*(b_g)$  higher than  $\pi^*(a_u)$ .

Figure 1 shows the low energy-loss region of the biacetyl spectrum between 2.0 and 7.0 eV at  $E_0 = 25$  eV and  $\theta = 10^\circ$  and  $90^\circ$ . In the  $10^\circ$  spectrum [Fig. 1(a)] one observes two low energy-loss features and a shoulder on the edge of a very intense band at about 7.0 eV. The lowest is the  $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$  transition with a measured onset at 2.67 eV, a maximum at 2.91 eV, and extending to 3.45 eV.<sup>19</sup> Lying between 3.82 and 5.28 eV with a maximum at 4.49 eV is a transition that *ab initio* SCF and CI results indicate should be designated  $\tilde{B}^1B_g \leftarrow \tilde{X}^1A_g$ .<sup>6</sup> The broadness of this band may be due to the presence of an enolic  $\pi \rightarrow \pi^*$  excitation.<sup>20</sup> The sharp peak at 6.24 eV is the first 3s member of an *s* Rydberg series converging to the lowest ionization potential, IP = 9.53 eV. As the scattering angle is increased three spin-forbidden features become apparent [Fig. 1(b)].<sup>21</sup> The lowest, overlapping greatly with the  $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$  band, has an onset at 2.28 eV and a maximum at 2.54 eV. It is attributed to a combination of the  $\tilde{a}^3B_u \leftarrow \tilde{X}^1A_g$  spin-forbidden excita-

tion,<sup>1</sup> previously seen in fluorescence experiments,<sup>2</sup> and a  $^3A_u \leftarrow ^1A_g$  excitation,<sup>19</sup> the latter being the dominant contributor. A second spin-forbidden band is seen in the region between 5 to 6 eV with a maximum at 5.47 eV. Calculations place several  $\pi \rightarrow \pi^*$  spin-forbidden transitions in this region,<sup>6,22</sup> particularly a  $^3B_u \leftarrow ^1A_g$  excitation predicted to be at 5.56 eV.<sup>22</sup> A last feature is observed at 5.80 eV and seems to be identifiable as the spin-forbidden counterpart of the 3s Rydberg excitation due to its relative sharpness.

The spectral region extending from 5 to 10 eV (just beyond the lowest IP) is shown in Fig. 2(a) under the optical conditions  $E_0 = 100$  eV and  $\theta = 3^\circ$ . All the transitions observed appear to be Rydberg in nature and indeed members of three series can be distinguished. Peaks at 6.24, 8.05, and 8.70 eV can be fit as the first three members of an *s* Rydberg series with a quantum defect  $\delta = 0.97$ . The *s* members are now much weaker than in the 25 eV spectra due to the fact that the  $n_g \rightarrow 3s$  transition is parity forbidden by dipole selection rules. The first two members of a *p* series at 7.21 and 8.42 eV are fit with  $\delta = 0.58$  and a feature at 7.72 eV is assigned to a 3*d* excitation. Transitions at 6.28 and 7.20 eV have been observed previously by Ells.<sup>3</sup>

## B. Acetylacetone (2,4-pentanedione)

As a room temperature vapor, acetylacetone consists of two structural isomers. One has the expected diketo molecular structure; however, acetylacetone exists predominantly as an enol.<sup>23,24</sup> In the diketo form the two highest occupied molecular orbitals have mostly oxygen nonbonding character and are labeled  $n_-$  (IP = 9.60 eV) and  $n_+$  (IP = 10.15 eV).<sup>23</sup> The highest occupied molecular orbitals in the enol compound are of  $\pi$  type (IP = 9.00 eV) and nonbonding type (IP = 9.60 eV).<sup>25</sup>

In Fig. 3 are shown spectra of acetylacetone between 3.0 and 6.0 eV energy loss at  $E_0 = 25$  eV and  $\theta = 10^\circ$  and  $90^\circ$ . At  $10^\circ$  [Fig. 3(a)] one sees a very strong band between 4.10 and 5.73 eV with a maximum at 4.70 eV. It is identified with the lowest spin-allowed  $\pi \rightarrow \pi^*$  transition in the enol molecule.<sup>24</sup> One also observes a weak band with an onset at 3.83 eV and maximum at 4.04 eV due to the first spin-allowed  $n \rightarrow \pi^*$  band in the acetylacetone diketo form.<sup>7,24,26</sup> An increase in scattering angle [Fig. 3(b)] reveals the presence of a spin-forbidden transition beginning at 3.15 eV with a maximum at 3.57 eV and overlapping with the diketo  $n \rightarrow \pi^*$  singlet-singlet (*S-S*) band. This feature can either be attributed to a  $\pi \rightarrow \pi^*$  singlet-triplet (*S-T*) excitation in the acetylacetone enol or possibly a  $n \rightarrow \pi^*$  (*S-T*) excitation in the acetylacetone keto form. An additional spin-forbidden excitation is evident at 5.52 eV and is assigned as a singlet-triplet 3s Rydberg excitation in the enol.

The 3.5 to 8.5 eV energy-loss region of the spectrum measured at  $E_0 = 100$  eV and  $\theta = 10^\circ$  is shown in Fig. 2(b). All the structure above 5.5 eV can be explained as being due to Rydberg transitions converging to the first IP of the enol. Indeed, peaks at 5.84 and 7.50 eV are the first two members of an *s* series with  $\delta = 0.93$ , peaks at 6.52 and 7.75 eV are the first members of a *p* series with  $\delta = 0.66$ , and peaks at 7.32 and 8.10 eV are the first members of *ad* series with  $\delta = 0.15$ .

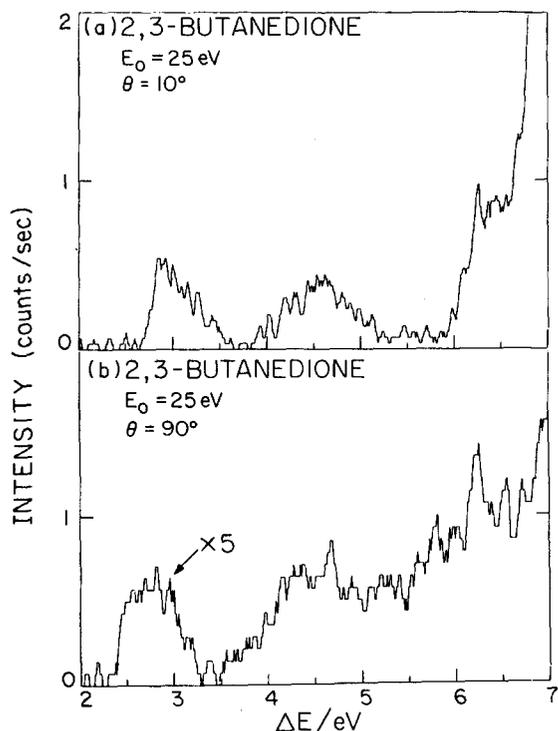


FIG. 1. 2,3-Butanedione (biacetyl) energy-loss spectra at an incident electron energy  $E_0 = 25$  eV and scattering angles: (a)  $\theta = 10^\circ$  and (b)  $\theta = 90^\circ$ . Incident electron current = 2 nA. Spectra are multiplied by any indicated expansion factors before plotting.

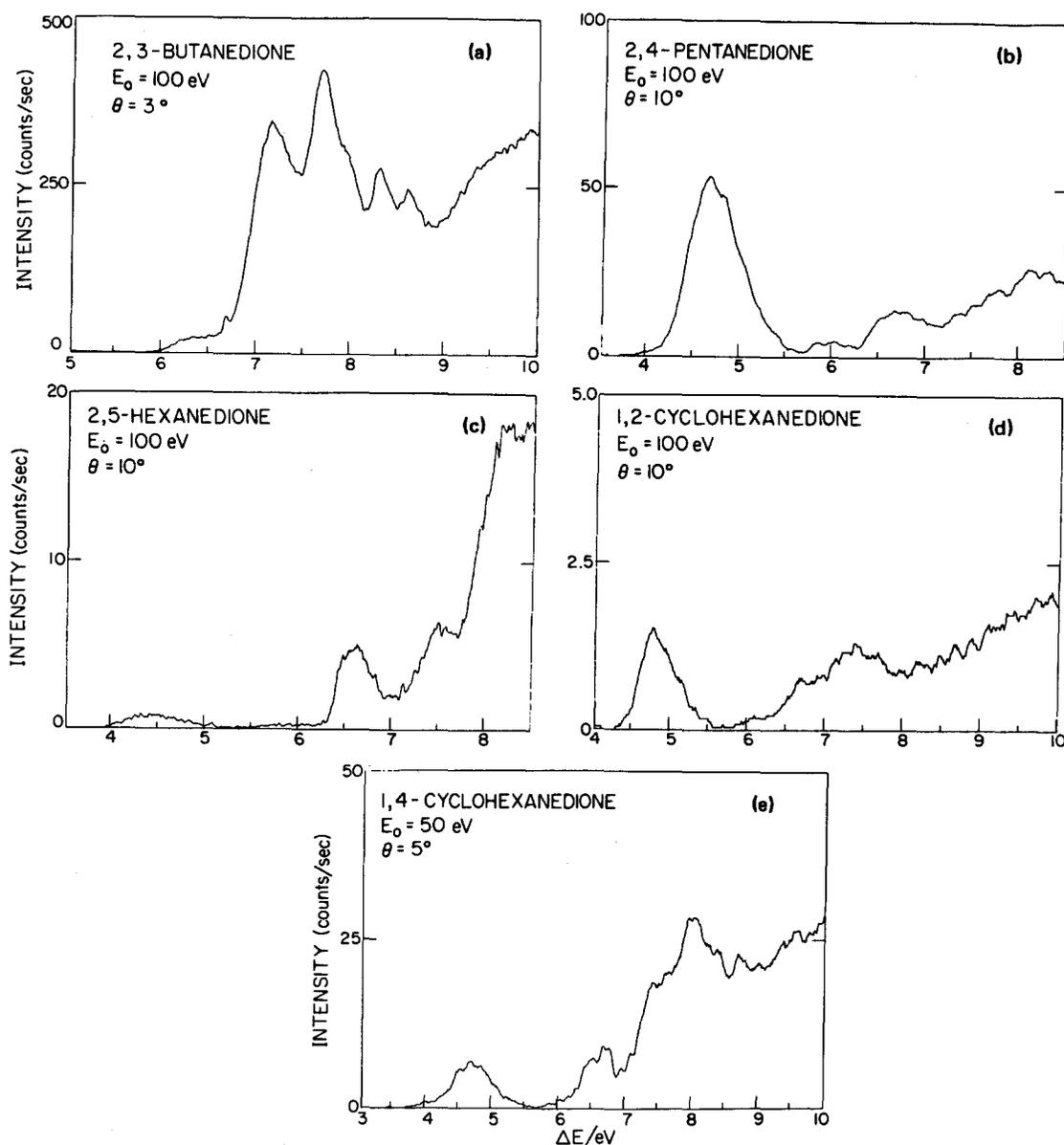


FIG. 2. (a) 2,3-Butanedione (biacetyl) energy-loss spectrum between 5.0 and 10.0 eV at  $E_0 = 100$  eV and  $\theta = 3^\circ$ . The peak at 6.67 eV is due to an Hg contamination in the vacuum system. (b) 2,4-Pentanedione (acetylacetone) energy-loss spectrum between 3.5 and 8.5 eV at  $E_0 = 100$  eV and  $\theta = 10^\circ$ . (c) 2,5-Hexanedione (acetylacetone) energy-loss spectrum between 3.5 and 8.5 eV at  $E_0 = 100$  eV and  $\theta = 10^\circ$ . (d) 1,2-Cyclohexanedione energy-loss spectrum between 4.0 and 10.0 eV at  $E_0 = 100$  eV and  $\theta = 10^\circ$ . (e) 1,4-Cyclohexanedione energy-loss spectrum between 3.0 and 10.0 eV at  $E_0 = 50$  eV and  $\theta = 5^\circ$ .

This disagrees with the assignment of Nakanishi *et al.*<sup>27</sup> who observed transitions at 7.4 and 8.08 eV and assigned, with the aid of a CNDO-CI calculation, the former as a valence  $\pi \rightarrow \pi^*$  excitation and the latter as a valence  $\sigma \rightarrow \sigma^*$  excitation.

### C. Acetylacetone (2,5-hexanedione)

The similarity between the ultraviolet absorption of 1,4-diketones and their corresponding monoketones is striking, suggesting that the two carbonyl groups in the diketones can be considered isolated in the ground and first excited states.<sup>10</sup> In fact, Schippers and Dekkers,<sup>13</sup> using a simple electrostatic model,<sup>28</sup> calculated that the splitting of the

$n \rightarrow \pi^*$  levels should only be  $50 \text{ cm}^{-1}$ . This calculation results in an underestimate of the splitting, however, because it neglects any through-bond interaction. Indeed, Dougherty *et al.*<sup>12</sup> using photoelectron spectroscopy found that for the (limited) group of 1,4-diketones they investigated the mean splitting of the nonbonding orbitals was 0.3 eV. This splitting is still relatively small, explaining why Schippers and Dekkers<sup>11</sup> found that the spectra of certain rigid, cyclic 1,4-diketones appeared very similar to those of the complementary monoketones.

The region of the acetylacetone spectrum between 2.5 and 6.5 eV is displayed in Fig. 4. At  $E_0 = 25$  eV and  $\theta = 10^\circ$  [Fig. 4(a)] one observes two broadbands and the onset of a

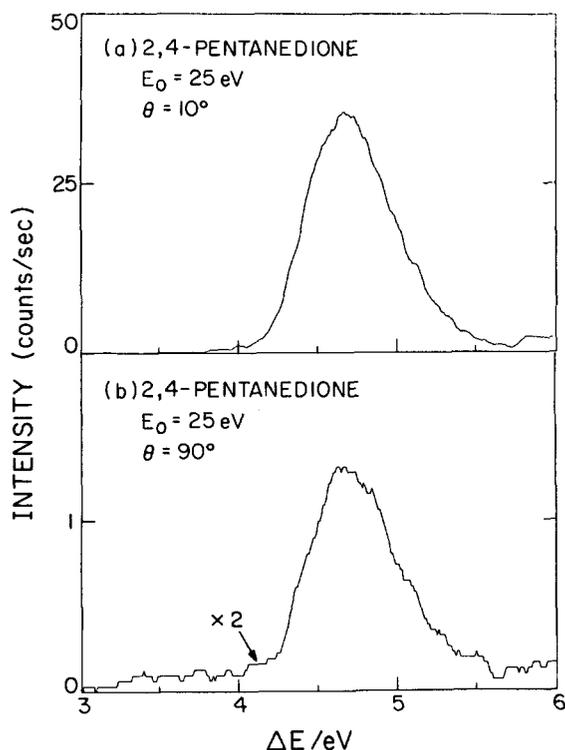


FIG. 3. 2,4-Pentanedione (acetylacetone) energy-loss spectra at an incident energy  $E_0 = 25$  eV and scattering angles: (a)  $\theta = 10^\circ$  and (b)  $\theta = 90^\circ$ . Incident electron current = 2 nA.

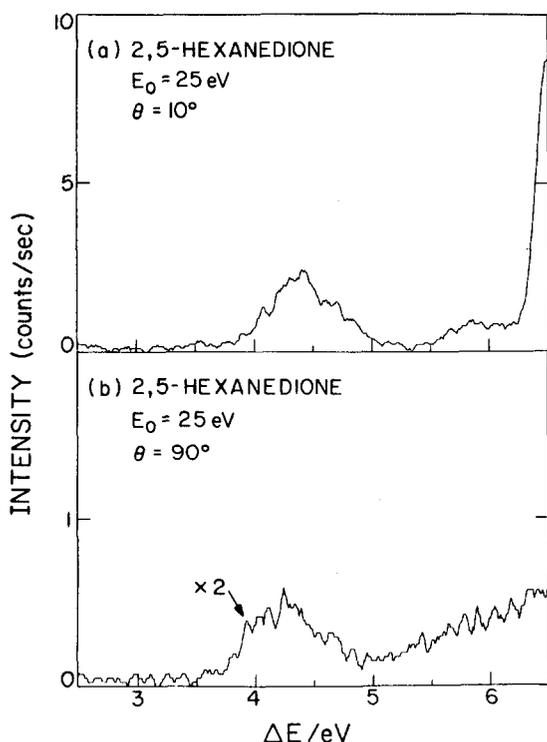


FIG. 4. 2,5-Hexanedione (acetylacetone) energy-loss spectra at an incident energy  $E_0 = 25$  eV and scattering angles: (a)  $\theta = 10^\circ$  and (b)  $\theta = 90^\circ$ . Incident electron current = 4 nA.

third. The lowest, between 3.97 and 5.15 eV with a maximum at 4.40 eV, can be assigned with confidence as the spin-allowed  $n \rightarrow \pi^*$  excitation. The second band onsets at 5.34 eV and possesses a maximum at 5.85 eV. Since the splitting between  $n, \pi^*$  states is expected to be very small, an assignment for this band is the lowest  $\pi \rightarrow \pi^*$  ( $S-S$ ) excitation. This transition is not observed in the smaller monoketones but expected to be at a relatively high energy loss (possible as high as 9.0 eV) superimposed by Rydberg bands.<sup>29</sup> The large peak beginning about 6.2 eV is the  $n \rightarrow 3s$  Rydberg excitation (*vide infra*). Increasing the scattering angle [Fig. 4(b)] produces two changes. The first is an apparent change in the onset and maximum of the spin-allowed  $n \rightarrow \pi^*$  transition to 3.55 and 4.16 eV, respectively. As previously discussed this is due to the presence of a relatively enhanced spin-forbidden  $n \rightarrow \pi^*$  transition. The second spectral change is the relative increase in intensity in the region between 5.15 to 5.34 eV also caused by a singlet-triplet contribution. A definitive band maximum is not obtained from the spectra.

The Rydberg portion of the acetylacetone spectrum is included in Fig. 2(c) which was measured under the optical conditions  $E_0 = 100$  eV and  $\theta = 10^\circ$  and spans the energy losses between 3.5 and 8.5 eV. In addition to those already mentioned, peaks are observed at 6.62, 7.49, and 8.17 eV. Assuming the transition at 6.62 eV corresponds to the  $n \rightarrow 3s$  excitation, the transition at 7.49 eV to the  $n \rightarrow 3p$  excitation, and the transition at 8.17 eV to the  $n \rightarrow 3d$  excitation, the best fit to the previously measured diketone (and ketone<sup>29,30</sup>) quantum defect is found using an ionization potential: IP = 9.95 eV. Specifically, for this IP one calculates  $\delta(n \rightarrow 3s) = 0.98$ ,  $\delta(n \rightarrow 3p) = 0.65$ , and  $\delta(n \rightarrow 3d) = 0.24$ . An additional peak was observed at 8.84 eV and is possibly due to an overlapping combination of higher Rydberg transitions.

#### D. 1,2-Cyclohexanedione

Even though 1,2-cyclohexanedione is exclusively in the ketonic form in the solid state,<sup>31</sup> it exists to a large extent in the enolic form in solution.<sup>32</sup> Calculations indicate that it may be primarily enolic in the gas phase as well.<sup>33</sup> Figure 5 shows spectra in the energy-loss region between 2.5 and 6.0 eV at  $E_0 = 50$  eV,  $\theta = 10^\circ$  and  $E_0 = 25$  eV,  $\theta = 50^\circ$ . The similarity between the spectrum of acetylacetone and 1,2-cyclohexanedione in this energy-loss region is striking. At  $E_0 = 50$  eV and  $\theta = 10^\circ$  [Fig. 5(a)] one sees an intense band between 4.34 and 5.70 eV with a maximum at 4.84 eV. As with acetylacetone, this band is assigned to the lowest spin-allowed  $\pi \rightarrow \pi^*$  enol transition. The weak band with an onset at 3.69 eV and maximum at 4.02 eV is due to the lowest spin-allowed  $n \rightarrow \pi^*$  transition of the ketonic form. Even though the orientation of the carbonyl groups is different than in biacetyl, one expects nearly the same energy difference (1.9 eV) between the  $n_+$  and  $n_-$  orbitals because of the dominance of the through-bond interaction.<sup>17</sup> Thus the second lowest spin-allowed  $n \rightarrow \pi^*$  transition should be at approximately 5.9 eV and obscured by enol Rydberg bands. An increase in scattering angle and decrease in incident electron energy [Fig. 5(b)] reveals the presence of a spin-forbidden band beginning at 2.70 eV with a maximum at 3.18 eV as

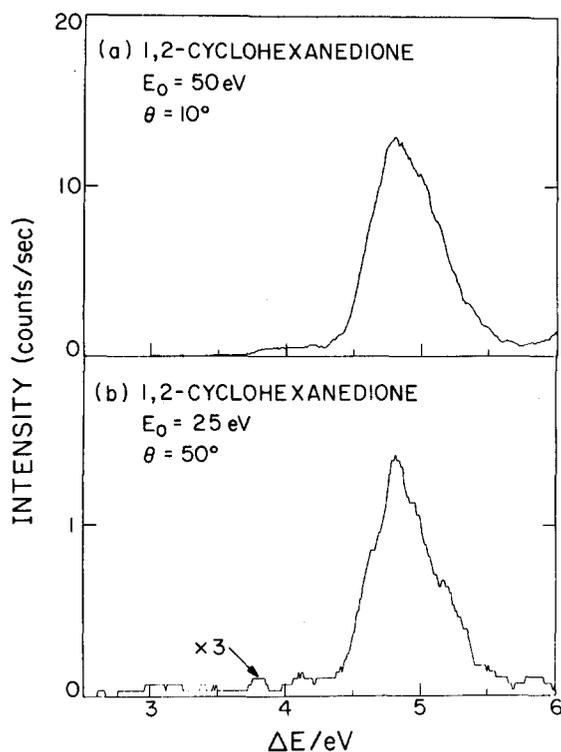


FIG. 5. 1,2-Cyclohexanedione energy-loss spectra at: (a)  $E_0 = 50$  eV and  $\theta = 10^\circ$  and (b)  $E_0 = 25$  eV and  $\theta = 50^\circ$ . Incident electron current = 0.5 nA.

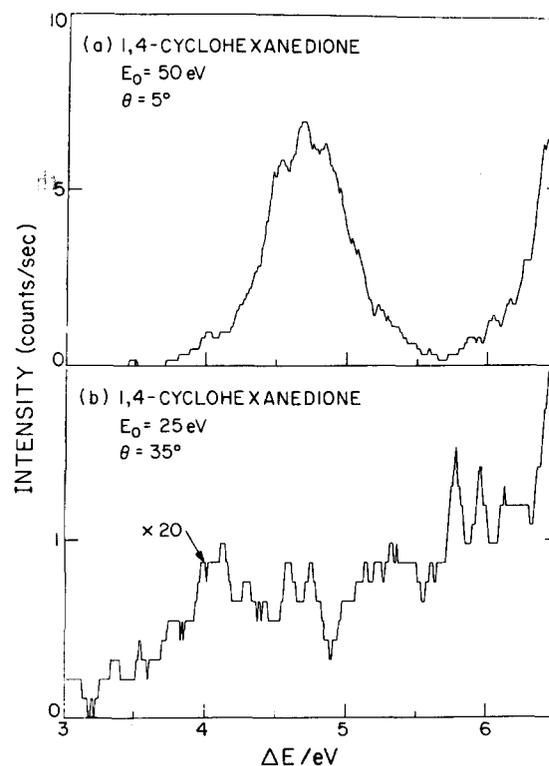


FIG. 6. 1,4-Cyclohexanedione energy-loss spectra at: (a)  $E_0 = 50$  eV,  $\theta = 5^\circ$  and (b)  $E_0 = 25$  eV,  $\theta = 35^\circ$ . Incident electron current = 5 nA.

signed as the lowest  $n \rightarrow \pi^*$  ( $S-T$ ) excitation of the ketonic form. The differential cross section (DCS) curves for these valence transitions confirm their spin-allowed or spin-forbidden nature.

The higher energy-loss region between 4 and 10 eV, at  $E_0 = 100$  eV and  $\theta = 10^\circ$ , is shown in Fig. 2(d). Only three distinct Rydberg bands are evident, located at 6.10, 6.92, and 7.48 eV. An ionization potential: IP = 9.40 eV is determined if one assumes the three bands are due to transitions to the 3s, 3p, and 3d orbitals and also assumes quantum defects  $\delta = 0.97, 0.66,$  and 0.34, respectively.

### E. 1,4-Cyclohexanedione

1,4-Cyclohexanedione has  $D_2$  symmetry (a "twist" configuration<sup>34</sup>) with coaxial carbonyl groups. Through-space interactions provide a minimum contribution, thus the splitting of the two highest occupied nonbonding orbitals is relatively small (0.2 eV) when compared to that in other 1,4-diketones,<sup>12,17</sup> with the measured ionization potentials being IP( $n_-$ ) = 9.65 eV and IP( $n_+$ ) = 9.85 eV.<sup>12</sup> Figure 6 shows the 3.0 to 6.5 eV energy-loss region of the 1,4-cyclohexanedione spectrum at  $E_0 = 50$  eV,  $\theta = 5^\circ$  and  $E_0 = 25$  eV,  $\theta = 35^\circ$ . The low intensity of the spectra arises from the relatively low sample pressure achieved for this compound at the scattering center (estimated to be  $\sim 2$  mTorr). Under optical conditions [Fig. 6(a)] one observes a band with an onset at 3.73 eV and a maximum at 4.68 eV. This is due to the  $n \rightarrow \pi^*$ ,  $^1A \leftarrow ^1A$  dipole symmetry-forbidden transition and has been seen previously in solution (maximum = 4.34 eV)<sup>35</sup> and low-temperature single crystals (onset = 3.89 eV,

maximum = 4.40 eV).<sup>36</sup> The onset of a broadband, which appears to be superimposed by a 3s Rydberg transition, is observed at 5.66 eV and may be due to the  $\pi \rightarrow \pi^*$ ,  $^1B_1 \leftarrow ^1A$  excitation. When the incident energy is lowered and the scattering angle increased [Fig. 6(b)] the  $n \rightarrow \pi^*$ ,  $^3A \leftarrow ^1A$  transition becomes evident, onsetting at 3.20 eV and maximizing at 4.13 eV. The presence of another spin-forbidden band with maximum at 5.78 eV is indicated. Contributions to the intensity may come from either the  $\pi \rightarrow \pi^*$ ,  $^3B_1 \leftarrow ^1A$  excitation or the  $n \rightarrow 3s$  ( $S-T$ ) Rydberg excitation.

The 1,4-cyclohexanedione spectrum under optical conditions [Fig. 6(a)] is extended to 10 eV energy loss in Fig. 2(e). Additional peaks are observed at 6.58, 7.36, and 7.95 eV. (The peak at 6.67 eV is due to an Hg impurity in the vacuum system.) Using an IP = 9.75 eV, the mean of IP( $n_-$ ) and IP( $n_+$ ),<sup>12</sup> assignments and quantum defects of  $n \rightarrow 3s$  ( $\delta = 0.93$ ) at 6.58 eV,  $n \rightarrow 3p$  ( $\delta = 0.61$ ) at 7.36 eV, and  $n \rightarrow 3d$  ( $\delta = 0.25$ ) at 7.95 eV are determined.

## IV. DISCUSSION AND CONCLUSIONS

As one might expect from previous results,<sup>10</sup> the energies of the lowest  $n \rightarrow \pi^*$  excitations for the acyclic diketones, as the distance between carbonyl groups increases, approach those of acetone. The lowest spin-allowed and spin-forbidden  $n \rightarrow \pi^*$  excitations are 2.91 and 2.54 eV for biacetyl, 4.04 and 3.57 eV for acetylacetone, 4.40 and 4.16 eV for acetonylacetone, and 4.38 and 4.18 eV for acetone.<sup>29,37</sup> The values for these transitions in 1,4-cyclohexanedione are also comparable to those for acetone, the lowest singlet-singlet and singlet-triplet  $n \rightarrow \pi^*$  excitations being 4.68 and 4.13 eV, re-

spectively. This trend appears to hold also for the lowest spin-forbidden  $\pi \rightarrow \pi^*$  excitation, at least as regards the band onsets (the most reproducible measure of the band positions); the onset is 5.15 eV for both acetylacetone and acetone.

The mean value for the singlet–triplet splitting of the  $n, \pi^*$  state in the acyclic diketones examined in this paper is 0.35 eV, a splitting comparable to the mean value of 0.30 eV for the small monocarbonyls formaldehyde, acetaldehyde, and acetone.<sup>29,38,39</sup> A remarkable contrast is provided by 1,2-cyclohexanedione, in which the singlet–triplet splitting for the  $n, \pi^*$  state is 0.84 eV. The singlet–triplet energy difference for a given electron orbital configuration results from the stronger correlation of electron motions in the triplet state than in the singlet state; i.e., the Pauli principle acts as a force minimizing electron–electron repulsion in the triplet state.<sup>40</sup> A simple qualitative analysis<sup>41</sup> reveals that the magnitude of the singlet–triplet energy splitting is proportional to the overlap integral of the initial and final orbitals. For a single carbonyl group oriented along the  $z$  axis, the highest occupied nonbonding orbital is represented by an oxygen  $p_y$  orbital and there is minimum overlap with the  $\pi$  and  $\pi^*$  orbitals, for which the  $yz$  plane is a nodal plane. This small  $n, \pi^*$  overlap also applies to the case of biacetyl. The highest occupied  $n$  orbital and lowest unoccupied  $\pi^*$  orbital are linear combinations of the corresponding isolated orbitals; however, since the carbonyl groups are oriented in a *trans* arrangement, the linear combinations of  $n$  and  $\pi^*$  orbitals overlap to the same small extent as in the monocarbonyls.

In 1,2-cyclohexanedione a different orientation may exist, due to the constraint imposed by the ring. Unlike the carbonyl groups in biacetyl, which lie in a plane, the two carbonyl groups in 1,2-cyclohexanedione can be twisted away from coplanarity. The overlap of the highest occupied  $n$  orbital (a linear combination of individual carbonyl nonbonding orbitals) with the lowest unoccupied  $\pi^*$  orbital (a linear combination of individual carbonyl  $\pi^*$  orbitals) would now be larger, thus a larger  $n, \pi^*$  singlet–triplet splitting. Whether the effect of the increased orbital overlap is enough to account for an increase of the  $n, \pi^*$  singlet–triplet splitting by a factor larger than 2 or whether additional factors are at play is uncertain.

In summary, the low-energy variable-angle electron energy-loss spectroscopy of five diketone compounds with varying carbonyl separations and orientations has been investigated. The increase in the number of bands compared to the monocarbonyls is in accord with the splitting caused by the through-bond interaction of like orbitals. Low-lying, spin-forbidden excitations have been observed and, in the case of 1,2-cyclohexanedione, a very large singlet–triplet splitting arises from an increased overlap of initial and final orbitals.

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- <sup>1</sup>K. Kaya, W. R. Harshbarger, and M. Robin, *J. Chem. Phys.* **60**, 4231 (1974).
- <sup>2</sup>G. M. Almy, H. Q. Fuller, and G. D. Kinzer, *J. Chem. Phys.* **8**, 37 (1940).
- <sup>3</sup>V. R. Eells, *J. Am. Chem. Soc.* **60**, 1864 (1938).
- <sup>4</sup>J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.* **77**, 6461 (1955).
- <sup>5</sup>G. Porter and M. W. Windsor, *Proc. R. Soc. London Ser. A* **245**, 238 (1958).
- <sup>6</sup>T.-K. Ha, *Chem. Phys. Lett.* **57**, 64 (1978).
- <sup>7</sup>G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Am. Chem. Soc.* **81**, 4682 (1959).
- <sup>8</sup>D. J. Pasto, D. M. Chipman, and J. J. Worman, *J. Phys. Chem.* **86**, 3981 (1982).
- <sup>9</sup>R. Hoffmann *Acc. Chem. Res.* **4**, 1 (1971).
- <sup>10</sup>E. A. Lissi, M. V. Encinas, F. Castañeda, and F. A. Olea, *J. Phys. Chem.* **84**, 251 (1980).
- <sup>11</sup>P. H. Schippers and H. P. Dekkers, *J. Am. Chem. Soc.* **105**, 145 (1983).
- <sup>12</sup>D. Dougherty, P. Brint, and S. P. McGlynn, *J. Am. Chem. Soc.* **100**, 5597 (1978).
- <sup>13</sup>P. H. Schippers and H. P. Dekkers, *J. Chem. Soc. Part 2* **1982**, 1429.
- <sup>14</sup>R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Am. Chem. Soc.* **92**, 706 (1970).
- <sup>15</sup>A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.* **72**, 3894 (1968); S. Trajmar, J. K. Rice, and A. Kuppermann, *Adv. Chem. Phys.* **18**, 15 (1970).
- <sup>16</sup>C. F. Koerting, Ph.D. thesis, California Institute of Technology, Pasadena CA 1985, and references therein.
- <sup>17</sup>D. O. Cowan, R. Gleiter, J. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem. Int. Ed.* **10**, 401 (1971).
- <sup>18</sup>S. P. McGlynn and J. L. Meeks, *J. Electron. Spectrosc.* **6**, 269 (1975).
- <sup>19</sup>G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966), p. 667.
- <sup>20</sup>D. Ben-Amotz and I. Y. Chan, *J. Phys. Chem.* **86**, 2428 (1982).
- <sup>21</sup>The relative differential cross section (DCS) for the elastic peak and inelastic features were obtained by a method described in the references of O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.* **59**, 6502 (1973); O. A. Mosher, M. S. Foster, W. M. Flicker, A. Kuppermann, and J. L. Beauchamp, *ibid.* **62**, 3424 (1975). In the case of severely overlapping bands, dividing points for calculating DCS's were chosen at a midpoint between the maxima. Due to the great deal of band overlap, all the 25 eV DCS curves exhibited some spin-forbidden behavior while the 50 eV curves exhibited distinct allowed or forbidden behavior.
- <sup>22</sup>J. M. LeClerecq, C. Mijoule, and P. Yvan, *J. Chem. Phys.* **64**, 1464 (1976).
- <sup>23</sup>J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.* **73**, 4553 (1951).
- <sup>24</sup>H. Nakanishi, H. Morita, and S. Nagakura, *Bull. Chem. Soc. Jpn.* **50**, 2255 (1977).
- <sup>25</sup>A. Schweig, H. Vermeer, and U. Weidner, *Chem. Phys. Lett.* **26**, 229 (1974).
- <sup>26</sup>R. S. Rasmussen, D. D. Tunnidiff, and R. R. Brattain, *J. Am. Chem. Soc.* **71**, 1068 (1949).
- <sup>27</sup>H. Nakanishi, H. Morita, and S. Nagakura, *Bull. Chem. Soc. Jpn.* **51**, 1723 (1978).
- <sup>28</sup>F. London, *J. Phys. Chem.* **46**, 305 (1942).
- <sup>29</sup>K. N. Walzl, C. F. Koerting, and A. Kuppermann (to be submitted).
- <sup>30</sup>D. C. Moule and A. D. Walsh, *Chem. Rev.* **75**, 67 (1975).
- <sup>31</sup>C. Duval and J. Lecomte, *Acad. Sci.* **254**, 36 (1962).
- <sup>32</sup>G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta* **30**, 663 (1947).
- <sup>33</sup>W. E. Noack, *Theor. Chem. Acta* **53**, 101 (1979).
- <sup>34</sup>P. Dowd, T. Dyke, and W. Klemperer, *J. Am. Chem. Soc.* **92**, 6327 (1970).
- <sup>35</sup>K. Ozeki, M. Inagaki, and J. Tanaka, *Bull. Chem. Soc. Jpn.* **42**, 3076 (1969).
- <sup>36</sup>K. Ozeki and J. Tanaka, *Bull. Chem. Soc. Jpn.* **42**, 3390 (1969).
- <sup>37</sup>W. M. St. John, R. C. Estler, and J. P. Doering, *J. Chem. Phys.* **61**, 763 (1974).
- <sup>38</sup>S. Taylor, D. Wilden, and J. Comer, *Chem. Phys.* **70**, 291 (1982).
- <sup>39</sup>W. M. St. John, R. C. Estler, and J. P. Doering, *J. Chem. Phys.* **61**, 763 (1974).
- <sup>40</sup>N. J. Turro, *Modern Molecular Photochemistry* (Benjamin-Cummings, Menlo Park, 1978), pp. 28–32.
- <sup>41</sup>S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.* **3**, 269 (1964).