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Double-ionization energies of some *n*-alkyl isocyanate molecules; studies with double-charge-transfer spectrometry and ab initio propagator theory

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Abstract

Double-charge-transfer (DCT) collisions of H^+, OH^+ and F^+ 3 keV beam ions with a series of alkyl isocyanate molecules were studied using mass spectrometric techniques. Measurement of the kinetic energies of H^- ions so produced enabled the determination of double-ionization energies (DIE) for transitions to singlet doubly ionized states of the target molecules; those for triplet doubly ionized states were obtained similarly from measurements of the kinetic energies of OH^- and F^- ions. Values up to approximately 40 eV were obtained in most cases and were found to be in close agreement with the predictions of ab initio calculations using propagator theory, also presented here. For *n*-butyl isocyanate (and by implication heavier molecules in the series) the density of doubly ionized states above 30 eV was both observed and predicted to be too large and featureless for meaningful analysis, so establishing an effective upper limit on molecular size for the current application of these techniques. Significant configuration interaction was predicted for the final doubly ionized states, which justified theoretical analysis with a relatively complex method that accounts well for correlation effects.

Keywords: Ionization energy; Propagator theory; Kinetic energy

1. Introduction

The techniques of double- and triple-charge-transfer spectrometry are well suited to the measurement of the energies of vertical multiple ionizations of the ground states of neutral gas-phase molecules to both stable and unstable states of their doubly and triply charged molecular ions, respectively. Each possible transition is directly related to an observable change in the kinetic energy of a high-energy (several keV) projectile ion when it undergoes a gas-phase collision with the neutral target molecule of interest [1]. Other well-established experimental techniques for the study of double ionization are gas-phase Auger spectroscopy [2] and a technique the development of which Beynon was closely associated with, charge-stripping [3]. The former allows examination of a wide range of double-ionization energies (DIEs) but experimental difficulties are often posed by the peaks being weak, broad and difficult to calibrate. Charge-stripping involves ionization of a molecular cation as it passes through a gas, so that cation must be stable for several microseconds if the second ionization is to have a significant probability of occurring. In either technique the transient molecular cation state may therefore have relaxed its geometry before the second ionization. In contrast, double-charge-transfer (DCT) transitions may be assumed vertical because the transit time in the collision region is very short, so the peaks in a DCT scan may be compared directly with the results of calculations of vertical DIEs. Additional advantages of DCT spectrometry are: the peak position resolution now achievable is typically 0.2–0.4 eV [4]; the spin multiplicity of the final dication states may be selected by an appropriate choice of projectile ion [1], so that separate scans may be obtained for singlet and triplet dication states. H^+, OH^+ and F^+ projectiles are normally used, for each of which the final anionic state of the projectile is a singlet, so that the singlet H^+ projectile populates singlet

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dication states, the triplet OH^+ and F^+ projectiles triplet dication states. Studies of singlet states with H^+ were initiated at Orsay [5] over 20 years ago, of triplet states with OH^+ and F^+ more recently at Swansea [1].

Here the results are reported of both DCT experimental and ab initio propagator theoretical studies of the valence DIEs of four members of an homologous series of quite large molecules that lack significant structural symmetries, the *n*-alkyl isocyanates, for which relatively complex manifolds of doubly ionized states are expected to exhibit relatively closely spaced energies and so a correspondingly greater challenge to the accuracy of experiment and theory. Of particular interest also are (i) the upper limit on the size of molecule that may usefully be studied and (ii) whether correlation effects, well accounted for in the theoretical approach used here, are significant enough to invalidate the approximate description of a doubly ionized state in terms of the removal of two electrons from a single pair of molecular orbitals.

2. Experimental

A DCT reaction may be represented by:

$$A^+ + M \rightarrow A^- + M^{2+}(n) \qquad (1)$$

where A^+ is the fast projectile ion, M is the neutral target molecule in its initial ground state and $M^{2+}(n)$ is a final dicationic stationary electronic state, If E_0 and E_n represent, respectively, the initial and final translational kinetic energies of A in this reaction with M, is the translational energy loss of the projectile:

$$E_0 - E_n = \mathrm{DIE}_n(\mathrm{M}) - E(A^+ \rightarrow A^-) \qquad (2)$$

is accounted for by the energy difference $\mathrm{DIE}_n(\mathrm{M})$, between $M^{2+}(n)$ and M, and the energy $E(A^+ \rightarrow A^-)$ released on the capture of two electrons by A^+, so that a plot of the magnitude of the A^- ion current against its final translational energy will exhibit a peak at each energy E_n that corresponds to population of a dication state $M^{2+}(n)$. Recoil and thermal energies of the target molecules in these reactions are negligible in comparison with the current best translational energy resolution of approximately 0.2 eV. A straightforward calibration of the E_n scale to yield DIEs directly is made possible by also measuring E_{Xe} for a similar DCT reaction of A^+ with xenon target atoms, that populates the lowest energy state of Xe^{2+} of spin multiplicity appropriate to the projectile A^+. Then:

$$E_0 - E_{\mathrm{Xe}} = \mathrm{DIE(Xe)} - E(A^+ \rightarrow A^-) \qquad (3)$$

which, using Eq. (2), yields:

$$\mathrm{DIE}_n(\mathrm{M}) - \mathrm{DIE(Xe)} = E_{\mathrm{Xe}} - E_n \qquad (4)$$

so eliminating the need for accurate values of E_0 and $E(A^+ \rightarrow A^-)$ because the required values of DIE(Xe) are known.

Both OH^+ and F^+ projectile ions were employed in the study of the DIEs to triplet dication states, since they provide information on different ranges of DIEs. The quantity $\mathrm{DIE}_n(\mathrm{M}) - E(A^+ \rightarrow A^-)$ is the ‘endoergicity’ of a DCT reaction; it has been established [1,6] that there is a ‘reaction window’ range of endoergicity outside which the probability of DCT reactions is relatively much smaller than for those with endoergicities within that window. $E(A^+ \rightarrow A^-)$ is about 14.8 eV for OH^+ projectiles, 20.8 eV for F^+ projectiles, the latter therefore extending the accessible range of triplet state DIEs.

The isocyanates used in the experiments were purchased from the Aldrich Chemical Company, quoted purities being greater than 97%. The H^+ and OH^+ ions were generated by electron impact of H_2O in the source of a Finnigan 8230 mass spectrometer (Finnigan MAT, Bremen, Germany). CF_4 was introduced into the source for the generation of F^+ ions.

The spectrometer was double-focusing with the magnet situated between the source and the electric sector, the configuration established by Beynon and coworkers as advantageous for Mass-analysed Ion Kinetic Energy Spectroscopy (MIKES) [7,8]. In conventional machines (electric sector followed by magnetic sector) ion fragmentations in the first field-free region could produce confusing spectra since the parent ions might be any of the molecular or fragment ions emerging from the source. On reversal of the order of the sectors [7,8] it became possible to select the parent ion in the magnetic sector; fragment ions produced in the second field-free region could then be energy analysed with the electric sector. In this work the positive projectile ions were accelerated to 3 keV translational energy and mass-selected to pass through a collision-gas cell located close to the intermediate focal point between the magnetic and the electric sector. DCT collisions with target molecules in this cell produced negative projectile ions which were transmitted to the detector through the electric sector. Scanning, through an appropriate range, of the voltage applied to the plates of the electric sector was equivalent to scanning the negative-ion translational energy (a known function of the applied voltage).

3. Theoretical

A theoretical analysis of the DIEs measured for a given molecule requires predictions to be made of the vertical energy differences between its initial neutral ground state and various final dication states, which are the stationary electronic states of the doubly charged ion having the initial geometric structure of the neutral molecule. A straightforward approach would be to perform separate calculations of the energies of the initial state and of each final state of interest, but an alternative procedure, much less computationally demanding, is to calculate the energy differences directly using a propagator method. Information required for the description of the double-ionization process is contained in the pp propagator, the equal-time 2-particle Green's function for the N-electron neutral molecule with both particles (electrons) created simultaneously at time t', and destroyed simultaneously at time t''. Matrix elements of the Fourier transform of the pp propagator for $t'' < t'$ take the form:

$$\prod\nolimits^{(-)}_{\mathrm{rs,tu}}(\omega) = \sum_{m\in(N-2)} \frac{x^{(m)}_{\mathrm{rs}}\, x^{(m)*}_{\mathrm{tu}}}{E^{N-2}_m - E^N_0 - \omega - i\varepsilon} \tag{5}$$

with $\varepsilon = 0^+$; this exhibits a pole wherever ω coincides with a DIE. r, s, t, u can be SCF molecular orbitals and m runs over all the stationary states of the $(N-2)$-electron dication. Here the ADC(2) method [9] has been followed to locate the pole energies. However, an ADC(2) calculation of the double-ionizations of the isocyanate molecules studied here, which have from 22 to 40 valence electrons, is computationally demanding even with one of the modest split-valence bases that have proved acceptable in ADC(2) calculations for smaller molecules. The geometric structures reported by Jones et al. [10] (the data reported for CH_3NCO were used to construct one for C_4H_9NCO) were adopted, with reflection symmetry in a molecular plane which gives the matrices block diagonal form; also, spin symmetry enables further block-diagonalization into singlet and triplet matrices. Nevertheless, the block matrices for the basis set of atom-centred functions used here have dimensions from about 2×10^4 for CH_3NCO, up to 3×10^5 for C_4H_9NCO, which would require the computation of a very large number of matrix elements and corresponding difficulty in calculating the required eigenvalues and their eigenvectors. Therefore the 'diagonal' ADC(2) approximation [11] has been adopted here as it is the physical basis of a novel and effective iterative computational technique [12] for the efficient calculation of the lower energy DIEs of interest to acceptable accuracy, using working matrices of dimension equal to the number of two-hole (2h) "main" basis configurations of the chosen symmetry. Tests of the diagonal approximation on a variety of small molecules [12], for which the DIEs had been previously calculated without it, indicated that its introduction resulted in systematic small reductions, typically 0.2 eV, in the DIEs of main transitions to dication states with significant 2h character, together with insignificant changes to the associated eigenvectors [12]. Its effects on the energies of transitions to satellite dication states with effectively no 2h character in contrast can exceed 1 eV [12] but, as such transitions are not anticipated to have significant cross sections in DCT processes, that poses no problem in this application.

Table 1
HF/6-311G** valence molecular orbital energies ε for the isocyanate molecules studied in this work

CH_3NCO		C_2H_5NCO		n-C_3H_7NCO		n-C_4H_9NCO	
M.O.	ε (eV)	M.O.	ε (eV)	M.O.	ε (eV)	M.O.	ε (eV)
						8a′	−39.29
						9a′	−35.99
						10a′	−34.57
				7a′	−39.33	11a′	−28.61
				8a′	−34.84	12a′	−25.26
				9a′	−33.00	13a′	−22.62
		6a′	−39.44	10a′	−26.61	1a″	−22.01
		7a′	−34.85	11a′	−22.04	14a′	−19.98
		8a′	−28.44	12a′	−20.24	15a′	−19.21
5a′	−39.51	9a′	−24.42	1a″	−20.18	16a′	−18.62
6a′	−34.83	10a′	−19.80	13a′	−19.22	2a″	−17.89
7a′	−26.93	11a′	−18.75	14a′	−17.90	17a′	−16.92
8a′	−20.83	1a″	−18.40	2a″	−17.60	18a′	−16.57
9a′	−18.74	12a′	−17.50	15a′	−16.98	3a″	−16.38
1a″	−18.00	2a″	−16.83	16a′	−16.09	19a′	−14.04
10a′	−17.97	13a′	−15.57	3a″	−15.93	4a″	−14.00
2a″	−16.28	14a′	−14.80	17a′	−13.42	20a′	−13.12
11a′	−15.79	3a″	−14.61	4a″	−12.28	5a″	−12.17
12a′	−12.30	15a′	−11.99	5a″	−11.34	21a′	−11.30
3a″	−11.51	4a″	−11.44	18a′	−11.22	6a″	−11.22
13a′	3.64	16a′	3.85	19a′	3.93	7a″	3.73
14a′	5.34	17a′	4.75	6a″	4.32	22a′	3.93
4a″	5.61	5a″	5.18	20a′	4.58	23a′	4.40
15a′	5.66	18a′	5.49	21a′	4.96	24a′	4.56
5a″	6.93	19a′	5.88	22a′	5.52	25a′	5.45
						8a″	6.15

The FORTRAN code for the iterative method has been linked with the Gaussian94 [13] molecular orbital program package, so as to employ the 1- and 2-electron matrix elements calculated in a molecular-orbital basis by that package. All computations were performed on a Pentium PC running under the Linux Red Hat operating system. A standard 6-311G** [13,14] valence-triple-zeta basis with a shell of polarization functions on each atom was employed. Following the initial SCF calculation to obtain the molecular orbitals of the neutral molecules (the SCF molecular orbital data are listed in Table 1), the post-SCF propagator calculations were carried out for double-ionizations to both singlet and triplet dication states, exploiting both spin and reflection symmetry to block-diagonalize the ADC(2) matrices. For each ADC(2) matrix block, its dimension and also the number of main 2h basis configurations of the same symmetry which determines the dimension of the much smaller working matrices that are repeatedly diagonalized instead [12], follow for each molecule:

CH_3NCO	17082, 42 ($^1A'$), 15984, 24 ($^1A''$), 23191, 31 ($^3A'$), 22239, 24 ($^3A''$)
C_2H_5NCO	47175, 65 ($^1A'$), 44840, 40 ($^1A''$), 65477, 51 ($^3A'$), 63288, 40 ($^3A''$)
C_3H_7NCO	105909, 93 ($^1A'$), 101508, 60 ($^1A''$), 149072, 76 ($^3A'$), 144688, 60 ($^3A''$)
C_4H_9NCO	207396, 126 ($^1A'$), 199794, 84 ($^1A''$), 294766, 106 ($^3A'$), 286824, 84 ($^3A''$)

Table 2
Double-ionization energies <45 eV of CH_3NCO for transitions to singlet states of its dication, calculated in the 'diagonal' ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.0	DCT (eV)
$^1A'$	29.11	85	73% $3a''^{-2}$	30.2	30.0 ± 0.3 (1)
$^1A''$	29.36	84	74% $12a'^{-1}3a''^{-1}$		
$^1A'$	30.47	84	69% $12a'^{-2}$	31.5	31.0 ± 0.2 (2)
$^1A''$	31.21	86	49% $11a'^{-1}3a''^{-1}$, 31% $2a''^{-1}12a'^{-1}$	32.2	32.1 ± 0.3 (3)
$^1A''$	32.70	82	26% $2a''^{-1}12a'^{-1}$, 24% $11a'^{-1}3a''^{-1}$	33.9	33.9 ± 0.3 (4)
$^1A'$	32.78	83	43% $11a'^{-1}12a'^{-1}$, 25% $2a''^{-1}3a''^{-1}$		
$^1A'$	33.10	83	39% $2a''^{-1}3a''^{-1}$, 23% $11a'^{-1}12a'^{-1}$		
$^1A''$	33.70	84	49% $10a'^{-1}3a''^{-1}$, 24% $1a''^{-1}12a'^{-1}$	34.7	34.9 ± 0.3 (5)
$^1A''$	34.38	82	35% $1a''^{-1}12a'^{-1}$, 23% $2a''^{-1}11a'^{-1}$	35.9	35.9 ± 0.4 (6)
$^1A'$	34.50	82	24% $1a''^{-1}3a''^{-1}$		
$^1A''$	34.63	84	62% $9a'^{-1}3a''^{-1}$		
$^1A'$	34.74	84	18% $11a''^{-2}$		
$^1A'$	34.93	84	40% $9a'^{-1}12a'^{-1}$		
$^1A''$	35.44	84	56% $8a'^{-1}3a''^{-1}$		
$^1A'$	36.06	82	34% $8a'^{-1}12a'^{-1}$, 24% $9a'^{-1}12a'^{-1}$	37.4	37.3 ± 0.3 (7)
$^1A''$	36.39	84	37% $1a''^{-1}11a'^{-1}$, 37% $10a'^{-1}2a''^{-1}$		
$^1A''$	36.69	73	31% $2a''^{-1}11a'^{-1}$		
$^1A'$	36.69	75	20% $11a'^{-2}$		
$^1A'$	37.46	75	19% $1a''^{-1}3a''^{-1}$	38.7	38.7 ± 0.5 (8)
$^1A''$	37.75	82	24% $8a'^{-1}2a''^{-1}$		
$^1A'$	37.89	81	26% $8a'^{-1}$, $11a'^{-1}$		
$^1A''$	38.72	79	24% $9a'^{-1}2a''^{-1}$, 20% $8a'^{-1}2a''^{-1}$	40.1	40.4 ± 0.4 (9)
$^1A'$	38.88	77	27% $9a'^{-1}11a'^{-1}$		
$^1A'$	39.36	71	30% $10a'^{-1}11a'^{-1}$		
$^1A''$	39.43	72	23% $10a'^{-1}2a''^{-1}$		
$^1A'$	40.00	84	51% $9a'^{-2}$	41.8	41.7 ± 0.3 (10)
$^1A'$	40.06	69	29% $1a''^{-2}$		
$^1A''$	40.10	77	30% $1a''^{-1}10a'^{-1}$, 20% $7a'^{-1}3a''^{-1}$		
$^1A'$	40.29	76	36% $10a'^{-2}$		
$^1A''$	40.62	75	29% $9a'^{-1}1a''^{-1}$		
$^1A'$	40.81	74	19% $9a'^{-1}10a'^{-1}$		
$^1A''$	41.17	71	56% $8a'^{-1}1a''^{-1}$		
$^1A'$	41.18	71	33% $8a'^{-1}10a'^{-1}$		
$^1A'$	41.56	76	19% $8a'^{-1}10a'^{-1}$		
$^1A''$	42.18	78	45% $7a'^{-1}3a''^{-1}$	43.3	43.1 ± 0.3 (11)
$^1A'$	42.32	77	46% $7a'^{-1}12a'^{-1}$		
$^1A'$	43.80	75	32% $8a'^{-1}9a'^{-1}$	44.7	
$^1A'$	44.93	64	34% $8a'^{-2}$	45.8	

Eigenvalues in the energy range up to 40 eV and above (32 eV for C_4H_9NCO), together with configuration weights >20% calculated from the corresponding eigenvectors, are listed in Tables 2–9 for comparison with the experimental data also presented there. Entries in italics are for satellites, here defined as having total 2h weight of <20%. In the diagonal ADC(2) approximation used here the interactions between different satellite configurations are neglected, resulting in DIEs for transitions to satellite states being predicted less accurately [12]. However, the DCT intensities of such transitions may be regarded as negligible [15], so that errors in their predicted energies are of no consequence in this investigation.

4. Discussion

Typical DCT scans for the double ionization of xenon with H^+ [16,17], OH^+ and F^+ [18] ions have been reported previously; data from those sources were used, together with singlet and triplet values of E_1(Xe) measured in this work, for calibration in Eq. (4). A typical DCT scan, for the collisions of H^+ with CH_3NCO, is shown in Fig. 1. Those peaks that are exhibited consistently in repeated scans (at least 10 for each projectile-target combination) are labelled (numerically for singlet states as in Fig. 1, alphabetically for triplet states) and represented the negative ion currents from reactions populating the dication states. The utility of employ-

Table 3
Double-ionization energies <45 eV of CH_3NCO for transitions to triplet states of its dication, calculated in the ‘diagonal’ ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.0	DCT (eV)
${}^3A''$	28.49	81	78% $12a'^{-1}3a''^{-1}$	29.5	29.9 ± 0.2 (A)
${}^3A'$	30.93	86	81% $2a''^{-1}3a''^{-1}$	32.1	32.4 ± 0.3 (B)
${}^3A''$	31.00	85	60% $11a'^{-1}3a''^{-1}$		
${}^3A'$	31.34	85	81% $11a'^{-1}12a'^{-1}$		
${}^3A''$	32.00	80	58% $2a''^{-1}12a'^{-1}$	33.0	33.5 ± 0.2 (C)
${}^3A''$	33.39	81	58% $10a'^{-1}3a''^{-1}$	34.6	34.3 ± 0.3 (D)
${}^3A'$	33.46	83	81% $1a''^{-1}3a''^{-1}$		
${}^3A''$	33.76	80	68% $1a''^{-1}12a'^{-1}$		
${}^3A''$	33.80	81	61% $9a'^{-1}3a''^{-1}$		
${}^3A'$	33.88	83	51% $10a'^{-1}12a'^{-1}$, 26% $9a'^{-1}12a'^{-1}$		
${}^3A'$	34.16	81	48% $9a'^{-1}12a'^{-1}$, 26% $10a'^{-1}12a'^{-1}$	35.2	35.2 ± 0.2 (E)
${}^3A''$	34.62	81	72% $8a'^{-1}3a''^{-1}$	36.1	36.1 ± 0.3 (F)
${}^3A'$	34.95	81	71% $9a'^{-1}12a'^{-1}$		
${}^3A''$	35.37	75	56% $2a''^{-1}11a'^{-1}$		
${}^3A''$	36.23	83	47% $1a''^{-1}11a'^{-1}$, 31% $10a'^{-1}11a'^{-1}$	37.5	37.3 ± 0.3 (G)
${}^3A'$	36.23	84	74% $10a'^{-1}11a'^{-1}$		
${}^3A'$	36.33	82	77% $1a''^{-1}2a''^{-1}$		
${}^3A''$	36.85	78	37% $9a'^{-1}2a''^{-1}$, 32% $8a'^{-1}2a''^{-1}$		
${}^3A'$	36.85	78	38% $9a'^{-1}11a'^{-1}$		
${}^3A''$	38.10	73	32% $10a'^{-1}2a''^{-1}$, 23% $1a''^{-1}11a'^{-1}$	39.1	38.7 ± 0.4 (H)
${}^3A'$	38.18	82	37% $8a'^{-1}11a'^{-1}$, 30% $9a'^{-1}11a'^{-1}$		
${}^3A''$	39.14	75	59% $1a''^{-1}10a'^{-1}$	40.3	39.7 ± 0.2 (I)
${}^3A'$	39.29	73	43% $9a'^{-1}10a'^{-1}$		
${}^3A''$	39.38	74	40% $9a'^{-1}1a''^{-1}$		
${}^3A'$	39.98	85	81% $8a'^{-1}9a'^{-1}$	41.1	40.8 ± 0.2 (J)
${}^3A''$	40.17	76	55% $8a'^{-1}1a''^{-1}$		
${}^3A'$	40.24	77	53% $8a'^{-1}10a'^{-1}$		
${}^3A''$	40.99	79	74% $7a'^{-1}3a''^{-1}$	42.2	41.9 ± 0.4 (K)
${}^3A'$	41.43	78	74% $7a'^{-1}12a'^{-1}$		
${}^3A'$	44.96	79	66% $7a'^{-1}11a'^{-1}$	46.0	

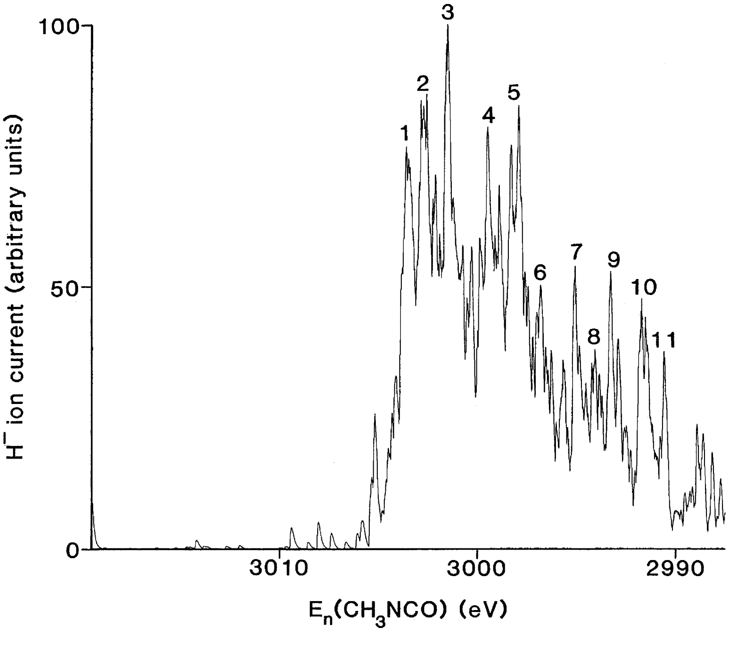

Fig. 1. A typical DCT scan for the reactions of 3 keV H^+ projectile ions with gaseous CH_3NCO molecules.

Table 4
Double-ionization energies <45 eV of C_2H_5NCO for transitions to singlet states of its dication, calculated in the ‘diagonal’ ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.0	DCT (eV)
$^1A''$	27.76	83	63% $15a'^{-1}4a''^{-1}$	29.2	29.1 ± 0.2 (1)
$^1A'$	27.93	84	48% $4a''^{-2}$, 27% $3a''^{-1}4a''^{-1}$		
$^1A'$	28.37	82	60% $15a'^{-2}$		
$^1A''$	28.67	84	49% $14a'^{-1}4a''^{-1}$, 29% $3a''^{-1}15a''^{-1}$		
$^1A''$	29.08	84	36% $3a''^{-1}15a''^{-1}$, 24% $13a'^{-1}4a''^{-1}$	30.3	30.1 ± 0.2 (2)
$^1A'$	29.46	83	38% $3a''^{-1}4a''^{-1}$, 24% $4a''^{-2}$		
$^1A'$	29.61	84	51% $14a'^{-1}15a'^{-1}$		
$^1A''$	30.56	82	40% $13a'^{-1}4a''^{-1}$	31.6	32.1 ± 0.2 (3)
$^1A'$	31.77	81	53% $13a'^{-1}15a'^{-1}$	33.0	33.0 ± 0.1 (4)
$^1A''$	31.92	81	59% $2a''^{-1}15a''^{-1}$		
$^1A''$	32.29	82	28% $12a'^{-1}4a''^{-1}$, 23% $13a'^{-1}3a''^{-1}$		
$^1A'$	32.66	83	26% $1a''^{-1}4a''^{-1}$, 22% $2a''^{-1}4a''^{-1}$	34.1	33.8 ± 0.2 (5)
$^1A'$	32.70	81	28% $2a''^{-1}3a''^{-1}$, 23% $2a''^{-1}4a''^{-1}$		
$^1A''$	32.85	82	31% $1a''^{-1}15a''^{-1}$, 23% $2a''^{-1}14a''^{-1}$		
$^1A'$	32.94	82	22% $13a'^{-1}14a'^{-1}$		
$^1A''$	33.17	81	No dominant configuration		
$^1A'$	33.31	82	23% $13a'^{-2}$, 22% $11a'^{-1}15a'^{-1}$		
$^1A''$	33.45	81	No dominant configuration		
$^1A'$	33.45	82	No dominant configuration		
$^1A''$	33.48	82	No dominant configuration		
$^1A'$	34.02	81	22% $11a'^{-1}15a'^{-1}$	35.2	34.9 ± 0.3 (6)
$^1A''$	34.08	82	39% $11a'^{-1}4a''^{-1}$		
$^1A'$	34.10	82	32% $3a''^{-2}$		
$^1A'$	34.31	81	20% $10a'^{-1}15a'^{-1}$		
$^1A''$	34.63	80	No dominant configuration	35.8	35.9 ± 0.3 (7)
$^1A'$	34.68	79	No dominant configuration		
$^1A''$	34.73	79	30% $14a'^{-1}3a''^{-1}$, 27% $12a'^{-1}3a''^{-1}$		
$^1A''$	35.03	82	41% $10a'^{-1}4a''^{-1}$		
$^1A'$	35.04	80	22% $14a'^{-2}$		
$^1A'$	35.34	77	23% $13a'^{-1}14a'^{-1}$	36.8	36.9 ± 0.2 (8)
$^1A''$	35.62	76	No dominant configuration		
$^1A''$	35.89	82	28% $11a'^{-1}3a''^{-1}$		
$^1A'$	36.16	73	No dominant configuration		
$^1A''$	36.18	78	No dominant configuration		
$^1A'$	36.29	80	27% $12a'^{-1}13a'^{-1}$		
$^1A'$	36.79	79	25% $10a'^{-1}13a'^{-1}$	37.9	38.0 ± 0.3 (9)
$^1A'$	36.97	75	21% $2a''^{-2}$		
$^1A''$	37.38	78	27% $12a'^{-1}2a''^{-1}$	38.7	39.0 ± 0.3 (10)
$^1A'$	37.50	77	28% $11a'^{-1}14a'^{-1}$		
$^1A''$	37.53	77	39% $9a'^{-1}4a''^{-1}$		
$^1A'$	37.72	78	22% $12a'^{-2}$		
$^1A''$	37.73	81	23% $10a'^{-1}1a''^{-1}$, 23% $10a'^{-1}2a''^{-1}$		
$^1A''$	38.00	79	24% $1a''^{-1}12a''^{-1}$		
$^1A'$	38.62	78	22% $11a'^{-1}12a'^{-1}$	40.0	40.1 ± 0.3 (11)
$^1A'$	38.79	73	No dominant configuration		
$^1A'$	38.82	77	No dominant configuration		
$^1A''$	38.89	76	No dominant configuration		
$^1A''$	38.94	72	29% $1a''^{-1}12a''^{-1}$		
$^1A'$	39.16	73	No dominant configuration		
$^1A'$	39.44	71	No dominant configuration		
$^1A'$	40.07	75	No dominant configuration	41.4	41.1 ± 0.2 (12)
$^1A''$	40.10	75	37% $11a'^{-1}1a''^{-1}$		
$^1A'$	40.32	69	22% $11a'^{-2}$		
$^1A''$	40.41	69	36% $10a'^{-1}1a''^{-1}$		
$^1A'$	40.67	75	25% $1a''^{-2}$		

Table 5
Double-ionization energies <45 eV of C_2H_5NCO for transitions to triplet states of its dication, calculated in the 'diagonal' ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.0	DCT (eV)
$^{3}A''$	27.21	81	72% $15a'^{-1}4a''^{-1}$	28.2	28.6 ± 0.2 (A)
$^{3}A'$	28.19	84	81% $3a''^{-1}4a''^{-1}$	29.4	29.4 ± 0.1 (B)
$^{3}A''$	28.51	83	58% $14a'^{-11}4a''^{-1}$, 20% $3a''^{-1}15a'^{-1}$		
$^{3}A''$	28.84	83	49% $3a''^{-1}15a'^{-1}$	29.9	30.4 ± 0.2 (C)
$^{3}A'$	28.91	82	77% $14a'^{-1}15a'^{-1}$		
$^{3}A'$	29.77	84	76% $13a'^{-1}15a'^{-1}$	31.4	31.5 ± 0.2 (D)
$^{3}A''$	29.96	81	54% $15a'^{-1}3a''^{-1}$		
$^{3}A'$	31.04	84	70% $2a''^{-1}4a''^{-1}$		
$^{3}A''$	31.50	80	64% $2a''^{-1}15a'^{-1}$	32.5	32.4 ± 0.2 (E)
$^{3}A''$	31.95	81	51% $12a'^{-1}4a''^{-1}$	33.1	33.2 ± 0.2 (F)
$^{3}A'$	32.03	81	66% $12a'^{-1}15a'^{-1}$		
$^{3}A'$	32.25	80	38% $2a''^{-1}3a''^{-1}$, 30% $1a''^{-1}4a''^{-1}$		
$^{3}A''$	32.50	78	33% $1a''^{-1}15a'^{-1}$	34.1	34.1 ± 0.2 (G)
$^{3}A''$	32.58	81	20% $13a'^{-1}3a''^{-1}$		
$^{3}A'$	32.61	80	46% $13a'^{-1}14a'^{-1}$		
$^{3}A''$	32.90	79	No dominant configuration		
$^{3}A'$	33.20	82	27% $10a'^{-1}15a'^{-1}$, 22% $11a'^{-1}15a'^{-1}$		
$^{3}A''$	33.23	82	No dominant configuration		
$^{3}A'$	33.36	82	40% $1a''^{-1}4a''^{-1}$, 29% $2a''^{-1}3a''^{-1}$		
$^{3}A''$	33.56	79	35% $11a'^{-1}4a''^{-1}$		
$^{3}A'$	33.63	81	29% $10a'^{-1}15a'^{-1}$, 27% $11a'^{-1}15a'^{-1}$		
$^{3}A''$	33.75	80	39% $14a'^{-1}3a''^{-1}$		
$^{3}A'$	34.00	81	25% $10a'^{-1}14a'^{-1}$	35.5	35.2 ± 0.3 (H)
$^{3}A''$	34.08	78	27% $10a'^{-1}4a''^{-1}$, 26% $12a'^{-1}3a''^{-1}$		
$^{3}A''$	34.36	77	No dominant configuration		
$^{3}A'$	34.59	79	37% $12a'^{-1}14a'^{-1}$		
$^{3}A''$	34.82	75	23% $2a''^{-1}13a'^{-1}$		
$^{3}A'$	35.01	80	48% $12a'^{-1}13a'^{-1}$		
$^{3}A'$	35.47	82	70% $1a''^{-1}3a''^{-1}$	36.8	36.3 ± 0.2 (I)
$^{3}A''$	35.69	80	35% $12a'^{-1}2a''^{-1}$, 27% $1a''^{-1}13a'^{-1}$		
$^{3}A''$	35.76	81	30% $11a'^{-1}3a''^{-1}$, 24% $1a''^{-1}14a'^{-1}$		
$^{3}A'$	35.82	76	26% $11a'^{-1}13a'^{-1}$, 25% $10a'^{-1}13a'^{-1}$		
$^{3}A'$	36.07	80	51% $11a'^{-1}14a'^{-1}$		
$^{3}A'$	36.41	80	77% $1a''^{-1}2a''^{-1}$	37.6	37.5 ± 0.3 (J)
$^{3}A''$	36.65	75	30% $12a'^{-1}2a''^{-1}$		
$^{3}A'$	36.75	80	37% $11a'^{-1}13a'^{-1}$, 27% $10a'^{-1}13a'^{-1}$		
$^{3}A''$	36.77	77	No dominant configuration		
$^{3}A''$	37.16	79	29% $9a'^{-1}4a''^{-1}$, 25% $10a'^{-1}2a''^{-1}$	38.8	38.8 ± 0.2 (K)
$^{3}A''$	37.43	79	39% $9a'^{-1}4a''^{-1}$		
$^{3}A''$	37.76	76	35% $1a''^{-1}12a'^{-1}$		
$^{3}A'$	37.81	78	68% $9a'^{-1}15a'^{-1}$		
$^{3}A'$	38.00	76	63% $1a''^{-1}2a''^{-1}$		
$^{3}A''$	38.08	75	30% $11a'^{-1}2a''^{-1}$		
$^{3}A'$	38.35	79	60% $10a'^{-1}12a'^{-1}$		
$^{3}A''$	38.95	72	28% $10a'^{-1}1a''^{-1}$, 23% $11a'^{-1}1a''^{-1}$	40.3	40.1 ± 0.5 (L)
$^{3}A'$	39.36	77	67% $10a'^{-1}11a'^{-1}$		
$^{3}A''$	39.66	76	36% $11a'^{-1}1a''^{-1}$, 31% $10a'^{-1}1a''^{-1}$		
$^{3}A''$	40.80	77	67% $8a'^{-1}4a''^{-1}$	41.9	41.1 ± 0.3 (M)
$^{3}A'$	40.97	77	33% $8a'^{-1}15a'^{-1}$		
$^{3}A''$	41.28	79	60% $9a'^{-1}3a''^{-1}$	42.4	42.4 ± 0.4 (N)
$^{3}A'$	41.44	78	35% $8a'^{-1}15a'^{-1}$, 33% $9a'^{-1}14a'^{-1}$		

Table 6
Double-ionization energies <40 eV of n-C_3H_7NCO for transitions to singlet states of its dication, calculated in the 'diagonal' ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^1A'$	25.30	85	78% $4a''^{-1}5a''^{-1}$	26.9	26.9 ± 0.3 (1)
$^1A''$	25.43	84	65% $5a''^{-1}18a'^{-1}$		
$^1A'$	25.58	83	71% $18a'^{-2}$		
$^1A''$	25.81	84	63% $4a''^{-1}18a'^{-1}$		
$^1A'$	28.00	83	66% $5a''^{-2}$	29.4	29.0 ± 0.3 (2)
$^1A''$	28.10	81	43% $17a'^{-1}5a''^{-1}$		
$^1A'$	28.88	81	34% $17a'^{-1}18a'^{-1}$	30.5	30.2 ± 0.2 (3)
$^1A''$	29.08	82	33% $17a'^{-1}4a''^{-1}$, 20% $16a'^{-1}4a''^{-1}$		
$^1A''$	29.17	83	28% $3a''^{-1}18a'^{-1}$		
$^1A'$	29.47	82	25% $16a'^{-1}18a'^{-1}$, 21% $17a'^{-1}18a'^{-1}$		
$^1A'$	29.56	80	40% $3a''^{-1}4a''^{-1}$, 34% $2a''^{-1}4a''^{-1}$		
$^1A''$	29.97	82	21% $2a''^{-1}18a'^{-1}$	31.3	31.2 ± 0.3 (4)
$^1A'$	30.06	83	28% $4a''^{-2}$		
$^1A''$	30.06	82	30% $16a'^{-1}4a''^{-1}$		
$^1A''$	30.45	82	30% $15a'^{-1}5a''^{-1}$	32.2	32.2 ± 0.2 (5)
$^1A'$	30.54	82	27% $15a'^{-1}18a'^{-1}$		
$^1A''$	30.71	81	49% $13a'^{-1}4a''^{-1}$		
$^1A'$	30.84	83	23% $15a'^{-1}18a'^{-1}$		
$^1A''$	30.85	80	No dominant configuration		
$^1A'$	30.96	82	30% $13a'^{-1}18a'^{-1}$		
$^1A'$	31.35	80	No dominant configuration		
$^1A'$	31.84	81	35% $2a''^{-1}4a''^{-1}$, 25% $3a''^{-1}4a''^{-1}$	33.4	33.4 ± 0.2 (6)
$^1A''$	31.91	82	27% $15a'^{-1}4a''^{-1}$		
$^1A''$	32.13	82	No dominant configuration		
$^1A''$	32.34	80	23% $14a'^{-1}5a''^{-1}$		
$^1A'$	32.44	80	30% $15a'^{-1}17a'^{-1}$, 24% $12a'^{-1}18a'^{-1}$		
$^1A''$	32.78	81	31% $2a''^{-1}17a'^{-1}$, 22% $1a''^{-1}18a'^{-1}$	34.1	34.3 ± 0.4 (7)
$^1A'$	32.79	80	44% $1a''^{-1}4a''^{-1}$		
$^1A'$	33.07	79	26% $16a'^{-2}$	34.7	35.1 ± 0.5 (8)
$^1A''$	33.17	80	29% $1a''^{-1}18a'^{-1}$		
$^1A'$	33.38	81	No dominant configuration		
$^1A''$	33.46	79	32% $13a'^{-1}5a''^{-1}$		
$^1A'$	33.49	79	No dominant configuration		
$^1A''$	33.64	80	No dominant configuration		
$^1A'$	33.79	80	26% $13a'^{-1}17a'^{-1}$		
$^1A''$	34.01	82	24% $12a'^{-1}5a''^{-1}$	35.7	36.1 ± 0.4 (9)
$^1A''$	34.12	80	31% $11a'^{-1}5a''^{-1}$		
$^1A''$	34.33	78	No dominant configuration		
$^1A'$	34.39	80	31% $11a'^{-1}18a'^{-1}$		
$^1A'$	34.50	81	No dominant configuration		
$^1A''$	34.54	79	No dominant configuration		
$^1A''$	34.76	79	No dominant configuration		
$^1A'$	34.77	79	22% $15a'^{-1}16a'^{-1}$		
$^1A''$	35.17	78	No dominant configuration	36.7	37.0 ± 0.1 (10)
$^1A'$	35.21	75	No dominant configuration		
$^1A'$	35.32	79	21% $15a'^{-2}$		
$^1A''$	35.59	77	23% $2a''^{-1}17a'^{-1}$		
$^1A'$	35.89	73	No dominant configuration	38.0	37.9 ± 0.1 (11)
$^1A''$	36.16	79	30% $13a'^{-1}3a''^{-1}$		
$^1A'$	36.19	81	No dominant configuration		
$^1A''$	36.23	78	28% $1a''^{-1}17a'^{-1}$		
$^1A'$	36.35	79	No dominant configuration		
$^1A'$	36.52	77	No dominant configuration		
$^1A'$	36.71	76	32% $2a''^{-1}3a''^{-1}$		
$^1A''$	36.97	77	23% $1a''^{-1}16a'^{-1}$		
$^1A'$	37.03	76	21% $14a'^{-1}16a'^{-1}$		
$^1A'$	37.12	77	29% $1a''^{-1}2a''^{-1}$		

Table 6 (*Continued*)

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^1A''$	37.15	78	No dominant configuration		
$^1A'$	37.45	75	No dominant configuration		
$^1A''$	37.50	77	30% $12a'^{-1}3a''^{-1}$		
$^1A'$	37.83	75	No dominant configuration	39.3	39.0 ± 0.1 (12)
$^1A''$	37.88	74	24% $14a'^{-1}2a''^{-1}$		
$^1A'$	37.88	75	No dominant configuration		
$^1A''$	38.07	79	38% $1a''^{-1}13a'^{-1}$		
$^1A'$	38.23	75	No dominant configuration		
$^1A''$	38.61	78	No dominant configuration	40.3	40.2 ± 0.3 (13)
$^1A'$	38.65	68	40% $2a''^{-2}$		
$^1A''$	38.77	76	No dominant configuration		
$^1A'$	38.86	76	21% $1a''^{-1}4a''^{-1}$		
$^1A'$	39.04	75	24% $11a'^{-1}16a'^{-1}$		
$^1A''$	39.17	76	No dominant configuration		
$^1A'$	39.24	77	No dominant configuration		
$^1A''$	39.30	77	27% $1a''^{-1}14a'^{-1}$		
$^1A'$	39.31	73	22% $12a'^{-1}14a'^{-1}$		
$^1A''$	39.35	3	97% $4a''^{-1}5a''^{-2}21a'^{1}$		
$^1A'$	39.64	75	32% $10a'^{-1}18a'^{-1}$	NB DIEs > 40 eV	
$^1A''$	39.72	69	No dominant configuration	Not calculated	
$^1A'$	39.74	2	96% $4a''^{-1}5a''^{-1}18a'^{-1}21a'^{1}$		
$^1A''$	39.80	77	46% $10a'^{-1}4a''^{-1}$		
$^1A'$	39.95	74	29% $11a'^{-1}13a'^{-1}$		

ing F^+ as well as OH^+ projectile ions is clear; the reaction window for F^+ is in a range of higher DIEs and there is consistency in the values of the DIEs for those peaks exhibiting significant intensity for both projectiles.

The detailed theoretical predictions indicate that, except for a few low-energy dication states, it is not possible to resolve individually, with the current experimental technique, most of the peaks associated with the dication states of these

Table 7
Double-ionization energies <40 eV of n-C_3H_7NCO for transitions to triplet states of its dication, calculated in the 'diagonal' ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^3A'$	25.12	84	81% $4a''^{-1}5a''^{-1}$	26.7	26.5 ± 0.3 (A)
$^3A''$	25.18	83	70% $5a''^{-1}18a'^{-1}$		
$^3A''$	25.63	83	66% $4a''^{-1}18a'^{-1}$		
$^3A'$	26.20	83	82% $17a'^{-1}18a'^{-1}$	27.5	27.9 ± 0.2 (B)
$^3A''$	27.51	79	57% $17a'^{-1}5a''^{-1}$	28.8	28.8 ± 0.2 (C)
$^3A''$	28.55	81	57% $17a'^{-1}4a''^{-1}$	30.1	29.8 ± 0.3 (D)
$^3A''$	28.95	82	24% $16a'^{-1}5a''^{-1}$, 22% $3a''^{-1}18a'^{-1}$		
$^3A'$	29.00	82	64% $16a'^{-1}18a'^{-1}$		
$^3A'$	29.30	80	33% $3a''^{-1}5a''^{-1}$, 25% $3a''^{-1}4a''^{-1}$	30.8	30.8 ± 0.3 (E)
$^3A'$	29.48	82	44% $3a''^{-1}5a''^{-1}$, 21% $3a''^{-1}4a''^{-1}$		
$^3A''$	29.54	80	40% $3a''^{-1}18a'^{-1}$		
$^3A''$	29.65	81	56% $16a'^{-1}4a''^{-1}$		
$^3A'$	29.65	81	34% $15a'^{-1}18a'^{-1}$		
$^3A''$	30.11	80	27% $2a''^{-1}18a'^{-1}$, 21% $15a'^{-1}5a''^{-1}$	31.8	31.8 ± 0.3 (F)
$^3A''$	30.30	81	22% $15a'^{-1}5a''^{-1}$		
$^3A'$	30.38	80	29% $15a'^{-1}18a'^{-1}$		
$^3A''$	30.50	81	53% $13a'^{-1}4a''^{-1}$		
$^3A'$	30.78	82	51% $13a'^{-1}18a'^{-1}$		
$^3A'$	31.15	81	45% $2a''^{-1}4a''^{-1}$, 32% $3a''^{-1}4a''^{-1}$	32.5	32.7 ± 0.2 (G)
$^3A''$	31.69	77	25% $3a''^{-1}17a'^{-1}$	33.5	33.7 ± 0.2 (H)
$^3A''$	31.76	79	35% $15a'^{-1}4a''^{-1}$		

Table 7 (*Continued*)

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^3A''$	31.83	81	30% $14a'^{-1}5a''^{-1}$		
$^3A'$	31.90	79	30% $16a'^{-1}17a'^{-1}$, 27% $14a'^{-1}18a'^{-1}$		
$^3A'$	31.96	82	48% $2a''^{-1}5a''^{-1}$, 25% $1a''^{-1}4a''^{-1}$		
$^3A'$	32.12	81	42% $15a'^{-1}17a'^{-1}$		
$^3A''$	32.41	78	52% $14a'^{-1}4a''^{-1}$		
$^3A''$	32.53	80	32% $2a''^{-1}17a'^{-1}$		
$^3A'$	32.73	80	49% $1a''^{-1}5a''^{-1}$, 23% $2a''^{-1}5a''^{-1}$		
$^3A''$	32.76	79	55% $13a'^{-1}5a''^{-1}$		
$^3A'$	32.79	78	20% $12a'^{-1}18a'^{-1}$		
$^3A''$	33.10	79	32% $1a''^{-1}18a'^{-1}$	34.6	34.7 ± 0.2 (I)
$^3A'$	33.21	80	41% $14a'^{-1}17a'^{-1}$		
$^3A''$	33.39	76	43% $12a'^{-1}5a''^{-1}$		
$^3A''$	33.52	75	30% $16a'^{-1}3a''^{-1}$		
$^3A'$	33.52	81	28% $15a'^{-1}16a'^{-1}$		
$^3A''$	33.84	80	40% $11a'^{-1}5a''^{-1}$	35.1	35.5 ± 0.2 (J)
$^3A'$	33.84	79	No dominant configuration		
$^3A''$	34.17	79	29% $11a'^{-1}5a''^{-1}$	36.0	36.4 ± 0.2 (K)
$^3A'$	34.35	80	37% $11a'^{-1}18a'^{-1}$		
$^3A''$	34.43	78	35% $12a'^{-1}4a''^{-1}$		
$^3A'$	34.65	80	70% $2a''^{-1}3a''^{-1}$		
$^3A'$	34.69	79	23% $12a'^{-1}17a'^{-1}$		
$^3A''$	34.77	80	29% $2a''^{-1}16a'^{-1}$		
$^3A'$	34.90	79	No dominant configuration		
$^3A''$	35.12	78	33% $2a''^{-1}15a'^{-1}$		
$^3A'$	35.16	80	29% $12a'^{-1}17a'^{-1}$		
$^3A''$	35.44	76	37% $13a'^{-1}3a''^{-1}$	37.2	37.3 ± 0.1 (L)
$^3A'$	35.66	80	31% $14a'^{-1}15a'^{-1}$		
$^3A''$	35.73	78	31% $1a''^{-1}17a'^{-1}$		
$^3A'$	35.74	81	73% $1a''^{-1}4a''^{-1}$		
$^3A'$	36.02	78	No dominant configuration		
$^3A''$	36.28	74	21% $1a''^{-1}17a'^{-1}$		
$^3A''$	36.62	76	35% $14a'^{-1}2a''^{-1}$	38.6	38.5 ± 0.4 (M)
$^3A'$	36.84	79	49% $1a''^{-1}3a''^{-1}$		
$^3A'$	37.03	80	49% $11a'^{-1}17a'^{-1}$		
$^3A''$	37.15	78	26% $1a''^{-1}16a'^{-1}$, 21% $12a'^{-1}3a''^{-1}$		
$^3A'$	37.30	76	20% $13a'^{-1}14a'^{-1}$		
$^3A''$	37.30	77	No dominant configuration		
$^3A''$	37.52	78	30% $11a'^{-1}4a''^{-1}$		
$^3A''$	37.73	76	No dominant configuration		
$^3A'$	37.80	76	37% $12a'^{-1}15a'^{-1}$		
$^3A'$	38.01	75	22% $12a'^{-1}15a'^{-1}$		
$^3A'$	38.32	79	50% $1a''^{-1}2a''^{-1}$, 27% $1a''^{-1}3a''^{-1}$	39.8	39.9 ± 0.3 (N)
$^3A''$	38.32	77	33% $11a'^{-1}3a''^{-1}$, 21% $11a'^{-1}2a''^{-1}$		
$^3A''$	38.40	76	No dominant configuration		
$^3A'$	38.44	76	62% $11a'^{-1}16a'^{-1}$		
$^3A''$	38.62	75	36% $12a'^{-1}2a''^{-1}$		
$^3A'$	38.86	76	70% $10a'^{-1}18a'^{-1}$	40.6	41.0 ± 0.3 (O)
$^3A'$	38.98	77	50% $12a'^{-1}14a'^{-1}$		
$^3A''$	39.12	75	63% $10a'^{-1}5a''^{-1}$	NB DIEs > 40 eV	
$^3A'$	39.13	0	100% $4a''^{-1}5a''^{-1}18a'^{-1}21a'^{1}$	Not calculated	
$^3A'$	39.16	81	69% $12a'^{-1}13a'^{-1}$		
$^3A''$	39.21	3	96% $4a''^{-1}5a''^{-2}21a'^{1}$		
$^3A''$	39.41	75	33% $1a''^{-1}15a'^{-1}$		
$^3A'$	39.54	78	47% $11a'^{-1}13a'^{-1}$		
$^3A''$	39.56	77	32% $10a'^{-1}4a''^{-1}$, 24% $1a''^{-1}14a'^{-1}$		
$^3A'$	39.68	0	100% $4a''^{-1}5a''^{-1}18a'^{-1}21a'^{1}$		
$^3A''$	39.73	75	32% $10a'^{-1}4a''^{-1}$		
$^3A'$	39.82	1	98% $4a''^{-1}5a''^{-1}18a'^{-1}21a'^{1}$		
					42.9 ± 0.4 (P)
					44.3 ± 0.3 (Q)

Table 8
Double-ionization energies <32 eV of n-C_4H_9NCO for transitions to singlet states of its dication, calculated in the 'diagonal' ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^1A'$	24.70	86	58% $5a''^{-1}6a''^{-1}$	26.2	26.2 ± 0.3 (1)
$^1A''$	24.78	84	38% $21a'^{-1}6a''^{-1}$, 37% $20a'^{-1}6a''^{-1}$		
$^1A''$	24.96	84	65% $5a''^{-1}21a'^{-1}$		
$^1A'$	25.09	83	55% $21a'^{-2}$		
$^1A''$	25.88	83	25% $20a'^{-1}6a''^{-1}$, 24% $19a'^{-1}6a''^{-1}$	27.3	27.2 ± 0.3 (2)
$^1A'$	26.20	83	44% $20a'^{-1}21a'^{-1}$		
$^1A'$	26.60	84	62% $4a''^{-1}6a''^{-1}$	28.1	28.3 ± 0.1 (3)
$^1A''$	26.95	83	66% $4a''^{-1}21a'^{-1}$		
$^1A''$	27.94	82	38% $19a'^{-1}6a''^{-1}$, 20% $20a'^{-1}5a''^{-1}$	29.3	29.1 ± 0.3 (4)
$^1A'$	28.08	82	50% $6a''^{-2}$		
$^1A'$	28.47	82	31% $19a'^{-1}20a'^{-1}$	No match attempted between theory and experimental values above 30 eV	
$^1A''$	28.67	81	33% $19a'^{-1}6a''^{-1}$		
$^1A'$	28.89	83	36% $3a''^{-1}5a''^{-1}$		30.2 ± 0.2 (5)
$^1A''$	28.99	83	51% $18a'^{-1}6a''^{-1}$		
$^1A''$	29.14	82	29% $3a''^{-1}20a'^{-1}$		
$^1A'$	29.25	83	35% $5a''^{-2}$		
$^1A''$	29.26	82	48% $18a'^{-1}5a''^{-1}$		
$^1A'$	29.35	82	38% $18a'^{-1}21a'^{-1}$		
$^1A'$	29.56	80	20% $19a'^{-1}21a'^{-1}$		
$^1A''$	29.73	82	No dominant configuration		31.0 ± 0.3 (6)
$^1A'$	29.91	82	No dominant configuration		
$^1A''$	30.06	83	No dominant configuration		
$^1A''$	30.18	82	No dominant configuration		
$^1A'$	30.20	82	34% $4a''^{-1}5a''^{-1}$		
$^1A'$	30.28	81	No dominant configuration		
$^1A'$	30.43	83	No dominant configuration		
$^1A''$	30.45	81	No dominant configuration		
$^1A''$	30.55	82	33% $19a'^{-1}4a''^{-1}$		
$^1A''$	30.86	81	No dominant configuration		
$^1A'$	30.91	81	No dominant configuration		
$^1A'$	31.03	82	33% $3a''^{-1}4a''^{-1}$		
$^1A''$	31.20	81	No dominant configuration		32.6 ± 0.3 (7)
$^1A'$	31.25	81	26% $20a'^{-2}$		
$^1A''$	31.38	80	23% $18a'^{-1}4a''^{-1}$		
$^1A''$	31.36	82	No dominant configuration		
$^1A'$	31.46	81	No dominant configuration		
$^1A'$	31.57	82	No dominant configuration		
$^1A'$	31.62	81	25% $3a''^{-1}6a''^{-1}$		
$^1A'$	31.94	81	No dominant configuration		

larger molecules. However, the theoretical DIE distribution for each molecule and spin multiplicity exhibits groups of states, separated by clear energy gaps, which should be consistent with the DCT peak distributions. Each DCT peak position may be matched with a calculated average DIE for a group of states (the midpoint energy for the group is used here) with which that peak may then be associated. Tables 2–9 list both the experimental results and computational predictions of the DIEs for the isocyanate molecules studied. As has proved to be the case in previous studies of other molecules, see for example, Refs. [15,19], the ADC(2) predictions of DIEs for a molecule require a uniform additive shift in energy to align them acceptably with the experimental values. The origin of this shift may be attributed to the ADC(2) approximation being equivalent [9] to a description of the initial and final states to second order perturbation theory which, for the neutral molecule ground state usually includes most, but not all, of the contributions to the correlation energy. As a consequence, the energy of the initial neutral state is, here implicitly, predicted to be a little higher than is actually the case. Such contributions to the excited states are much more random in their effects, so a systematic small reduction in the predicted transition energies may be expected with the ADC(2) approximation.

Shifts of +1.0 eV (CH_3NCO, C_2H_5NCO) and +1.3 eV (C_3H_7NCO, C_4H_9NCO) appear to be optimal and consistent with the above argument. Once applied, the relative energy separations of the experimentally observed peak structure and the groups or bands of predicted DIEs tally very well, usually well within the experimental uncertainties. At higher energies above 30 eV, especially for the larger molecules, it is clear that there are places in the tables where alternative

Table 9
Double-ionization energies <32 eV of *n*-C_4H_9NCO for transitions to triplet states of its dication, calculated in the ‘diagonal’ ADC(2) approximation (see text) and measured with double-charge-transfer spectroscopy

Term	DIE (eV)	Main (%)	Leading configuration weights	Group DIE (eV) + 1.3	DCT (eV)
$^{3}A'$	24.53	85	81% $5a''^{-1}6a''^{-1}$	26.4	26.9 ± 0.2 (A)
$^{3}A''$	24.63	84	44% $21a'^{-1}6a''^{-1}$		
$^{3}A''$	24.84	84	65% $5a''^{-1}21a'^{-1}$		
$^{3}A'$	25.26	84	75% $20a'^{-1}21a'^{-1}$		
$^{3}A''$	25.66	83	32% $20a'^{-1}6a''^{-1}$, 22% $21a'^{-1}6a''^{-1}$		
$^{3}A'$	26.48	83	76% $4a''^{-1}6a''^{-1}$	27.9	27.8 ± 0.3 (B)
$^{3}A'$	26.64	82	74% $19a'^{-1}21a'^{-1}$		
$^{3}A''$	26.79	82	67% $4a''^{-1}21a'^{-1}$		
$^{3}A''$	27.74	81	35% $19a'^{-1}5a''^{-1}$	29.2	28.8 ± 0.3 (C)
$^{3}A''$	28.01	79	39% $19a'^{-1}6a''^{-1}$		
$^{3}A'$	28.53	81	62% $19a'^{-1}20a'^{-1}$	30.2	29.7 ± 0.3 (D)
$^{3}A'$	28.73	82	33% $3a''^{-1}5a''^{-1}$, 32% $4a''^{-1}5a''^{-1}$		
$^{3}A''$	28.76	82	59% $17a'^{-1}6a''^{-1}$		
$^{3}A''$	28.93	82	30% $20a'^{-1}5a''^{-1}$, 20% $19a'^{-1}5a''^{-1}$		
$^{3}A''$	28.97	82	No dominant configuration		30.8 ± 0.3 (E)
$^{3}A'$	29.03	81	60% $17a'^{-1}21a'^{-1}$		
$^{3}A''$	29.12	81	54% $18a'^{-1}5a''^{-1}$		
$^{3}A'$	29.16	81	39% $18a'^{-1}21a'^{-1}$, 22% $18a'^{-1}20a'^{-1}$		
$^{3}A'$	29.24	82	42% $4a''^{-1}5a''^{-1}$		
$^{3}A''$	29.74	80	22% $4a''^{-1}20a'^{-1}$	31.3	31.6 ± 0.2 (F)
$^{3}A''$	29.89	81	28% $3a''^{-1}21a'^{-1}$, 20% $3a''^{-1}20a'^{-1}$		
$^{3}A'$	29.91	83	63% $3a''^{-1}6a''^{-1}$		
$^{3}A''$	30.01	82	25% $15a'^{-1}5a''^{-1}$		
$^{3}A'$	30.14	81	40% $18a'^{-1}20a'^{-1}$, 22% $18a'^{-1}21a'^{-1}$		
$^{3}A'$	30.23	82	No dominant configuration		
$^{3}A''$	30.32	81	30% $19a'^{-1}4a''^{-1}$		
$^{3}A''$	30.61	80	26% $18a'^{-1}6a''^{-1}$	32.3	32.2 ± 0.2 (G)
$^{3}A''$	30.79	79	30% $2a''^{-1}21a'^{-1}$		
$^{3}A'$	30.94	80	57% $3a''^{-1}4a''^{-1}$		
$^{3}A''$	31.00	81	37% $17a'^{-1}5a''^{-1}$		
$^{3}A'$	31.11	80	21% $15a'^{-1}21a'^{-1}$		
$^{3}A''$	31.12	81	48% $18a'^{-1}4a''^{-1}$		
$^{3}A'$	31.23	81	No dominant configuration		
$^{3}A'$	31.26	81	45% $2a''^{-1}5a''^{-1}$, 24% $3a''^{-1}5a''^{-1}$		
$^{3}A'$	31.37	81	26% $17a'^{-1}20a'^{-1}$, 26% $14a'^{-1}21a'^{-1}$		
$^{3}A''$	31.74	79	27% $16a'^{-1}6a''^{-1}$	No match attempted between theory and experimental values above 33 eV	33.1 ± 0.3 (H)
$^{3}A''$	31.87	81	29% $2a''^{-1}21a'^{-1}$, 21% $3a''^{-1}21a'^{-1}$		
$^{3}A'$	32.00	78	27% $14a'^{-1}21a'^{-1}$		

groupings of the theoretical DIEs might be acceptable. For C_4H_9NCO the number of valence electrons is large enough to result in a very large density of dication states which does not exhibit enough significant structure at higher energy to facilitate sensible groupings. Above 30 eV for singlets and 32 eV for triplets, the theoretical DIE distributions are dense and quasi-continuous and therefore are not reported here above 32 eV (although calculations up to 36 eV were performed), as they provide no useful insight into the similarly featureless associated experimental data.

Most of the doubly ionized states reported in the tables exhibit a significant degree of configuration interaction associated with the systematic inclusion of correlation effects to second order in the ADC(2) theory [13]. The weights of the dominant configurations for each state listed are, in general, much below 100%, showing that simpler theoretical analysis based on a single-configuration orbital-pair model of each doubly ionized state will in general not be well suited to these molecules. In such an orbital-pair model the energy to create a doubly ionized state is the sum of the energies required to remove two electrons from the orbitals they occupy and a repulsive interaction energy between the two positive ‘holes’ thus created. The latter energy would be expected to be comparatively smaller for larger molecules because of the greater average separation of the holes; although detailed calculation of this energy is not sensible here because correlation effects mix significantly various orbital pairs into these doubly ionized states, trends that reflect its concept may be identified in the tables, for example, the lowest calculated DIEs (in eV) are, with increasing molecular size: for singlet states, 29.11, 27.96, 25.30, 24.70; for triplet states, 28.49, 27.21, 25.12, 24.53.

Overall, the consistent agreement between DCT experiment and ADC(2) theory for this series of larger molecules is very good and indicates that both the experimental and theoretical methods used here are reliable. However, this investigation does indicate that, while the doubly ionized states of molecules of relatively complex low-symmetry structure may be investigated with them, increases in either the range of DIEs examined or the size of the molecules studied will encounter the natural limit to their useful application, above which the distribution of DIEs becomes effectively continuous. Here, C_4H_9NCO with 28 valence electrons was found to have distinguishable features both experimentally and theoretically only for DIEs less than 30 eV; this effectively indicates the current limit on the size of organic molecule to which these methods may be sensibly applied.

5. Appreciations

The achievements of Professor John Beynon in the field of mass spectrometry are too well recognized to need further acclamation here. All the authors have, in different ways, been the fortunate beneficiaries of his leadership, particularly in being associated with the Mass Spectrometry Research Unit he established at Swansea. Both I.W.G. and, later, M.A.B. were research students there; D.E.P., whose collaboration with F.M.H. began soon after J.H.B. had officially retired from the Unit (but not of course from the occasional check on the workers!), happily recalls the calm and positive encouragement J.H.B. gave him as he became involved with an extended and fruitful project.

It is appropriate here for colleagues of Professor Frank Harris to record their appreciation of him as a fine research leader, colleague and friend. Sadly, he lost his brave battle with motor-neurone disease soon after his work for this paper was completed. He joined the Unit shortly after its formation and his enthusiasm for, and achievements in, mass spectrometry continued throughout his career there. He would have insisted on submitting a contribution to this special issue in honour of J.H.B. and his co-authors are glad that this can still be so.

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