

Comment on: Infrared plus vacuum ultraviolet spectroscopy of neutral monomers and clusters

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A recently presented action spectroscopy approach to obtain size-specific IR spectra of molecular clusters without suitable UV chromophore is analysed in terms of available direct absorption results.

In a series of recent papers in this journal,¹⁻⁴ an interesting and promising IR spectroscopic tool was presented and applied to simple alcohols and organic acids and their neutral and ionic clusters. It is size-specific even for neutral clusters which lack a suitable UV chromophore for soft resonant ionization, at least in favorable cases. For such systems, direct absorption techniques⁵ (which lack size-specificity) or crossed beam techniques⁶ (which lack simplicity) have up to now been the methods of choice. Like for any indirect ‘action’ spectroscopy, it is advisable to compare the results obtained by the new technique to linear, direct absorption results, if they are available. This ensures that there are no major distortions of the spectral response compared to a one-photon IR absorption event, which is the quantity most easily accessible to quantum theoretical treatments. The purpose of this comment is to carry out such a comparison with mostly published data, as that appears not to have been done in sufficient detail in the original papers.¹⁻⁴ Only neutral monomers and clusters and only $\approx 3\mu\text{m}$ transitions will be addressed.

The proposed monomer technique¹⁻⁴ (nonresonant ionization detected or NRID-IR spectroscopy) is straightforward. The VUV laser photon alone is either not (methanol, acetic

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acid, propionic acid) or just barely (ethanol) able to ionize the molecule. Vibrational excitation of the molecule by a preceding IR laser opens either the ionization channel or additional ion fragmentation channels. In the latter case (NRIFD-IR), the new fragment ions are monitored. Table 1 compares the reported monomer wavenumbers obtained by this scheme with direct absorption jet FTIR results and other linear spectroscopy data. For methanol, where the complex torsional-rotational structure has led to diverging band center determinations (see Ref. 7 and references cited therein), the NRI band center is close to the best available values.⁷ For ethanol monomer, the NRIFD-IR values are shifted by 4-7 cm⁻¹ from established⁸ and recently refined values^{7,9} employing linear techniques. This discrepancy is small enough to be caused by calibration, thermal broadening, band overlap or other secondary factors of influence. However, it may also be related to the fact that in this case the VUV excitation already leads to ionization. For acetic acid, the match between the NRIFD-IR^{3,4} value and other sources (see Ref. 10, which is cited as Ref. 18 and as Ref. 46 in Ref. 3) for the OH stretching fundamental is again perfect. More interesting is the comparison for dimers, where the non-resonant ion dip infrared (NRIDip) technique was applied. VUV excitation is above the ionization threshold in the investigated cases, but the preceding IR laser can induce dissociation of the dimer, by absorption of either one or typically more photons. This process depletes the ion signal and the wavenumber dependence of the depletion is interpreted as the vibrational spectrum. Table 2 compares the NRIDip results with direct absorption and other available data from linear spectroscopy.

The methanol dimer donor band is somewhat broad, but only slightly too low or too high^{5,11} if the values given in the text or in table I of Ref. 1 (with switched footnotes) are used. The ethanol dimer donor NRIDip band is broad and unstructured. More importantly, it sits on the slope of an even broader feature which has the opposite sign, i.e. the IR excitation enhances ionization instead of depleting it. The fact that the depletion signal is now blue-shifted by more than 30 cm⁻¹ from the narrow and well structured, true direct absorption or Raman band,^{7,9,11,12} is probably related to this artifact.

The most likely explanation is that depletion of dimers due to IR excitation and enhancement of dimers due to IR trimer (and larger cluster) excitation with subsequent predissociation overlap in the spectrum. Therefore, the low frequency wing of the dimer is cancelled by the high frequency wing of the trimer, inducing an apparent blue-shift in the band maximum of the former. A prerequisite for such a spectral overlap already in

the dimer is the extreme spectral broadening observed in the NRI experiments on alcohol clusters. Apparently, internally hot clusters show a more favorable cross section for non-resonant ionization after IR excitation than the cold ones which are certainly dominant in the expansion. This may be related to a significant role of multi-photon processes in the IR excitation step. On the other hand, it may also contribute to the observed blue shift relative to direct absorption spectra.

For acetic acid dimer, where more than one IR photon is clearly needed for dissociation, the deviation between direct absorption^{13,14} (in contrast to the statement in Ref. 3, this is also a supersonic jet study and not a room temperature investigation) and NRI spectra is smaller (see table 2), but comparable to the width of the bands. A systematically increasing deviation of 8-14 cm⁻¹ between 2500 and 2800 cm⁻¹ for the Fermi resonance modes ν_{FR} ¹³⁻¹⁵ drops to 4 cm⁻¹ for the band with dominant OH stretching character ν_{OH} near 2926 cm⁻¹. For several bands, the vibrational assignment suggested by Hu et al.³ in terms of combination bands with van der Waals modes does not correspond to the accepted interpretation.^{14,15}

For methanol and ethanol trimers and tetramers, the deviations between the NRI results and direct absorption data^{5,11,12} for the OH stretching fundamentals become very large and systematic, on the order of +50 cm⁻¹. Also, the bands are much broader than in direct absorption, sometimes by an order of magnitude. The most likely reason is again a combination of process-induced thermal excitation and interference from fragmentation of higher clusters, which cancels or even inverts the depletion effect in a complex, frequency-dependent manner. Fragmentation interference is mentioned when discussing Fig. 3 (erroneously quoted as Fig. 4) in Ref. 1 in the context of methanol trimer. Laser fluence and expansion conditions (carrier gas) may have an influence, as the methanol tetramer band was observed in the correct position in a similar study by the same authors¹⁶ (cited incorrectly as Ref. 21 in Ref. 1, the incorrect citation being itself incorrect in year, volume and page number). Even larger band center differences for methanol oligomers beyond the tetramer between the two size-specific studies of the authors^{1,16} remain uncommented.

The jet-FTIR technique employed in our group^{11,13} may be unconventional in terms of the dimensions of pulse length, background pressure and probe volume within the zone of silence. Several comparisons to laser absorption techniques,^{5,12} to skimmed molecular beam spectra,⁶ and to our new Raman setup,⁷ which only probes a tiny slice of the jet, have been made. They leave no doubt that jet-FTIR spectroscopy provides a correct,

well-calibrated, and highly reproducible picture of cold, ground state cluster dynamics and absorption cross sections, as it is essential for the comparison to quantum-chemical calculations.¹⁵

Whatever the final interpretation of the NRI experiments for neutral cluster spectra will be, comparison to direct absorption spectroscopy shows promise in providing important clues towards the underlying mechanism of this high energy process.

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Table 1: Comparison of NRI(F)D-IR transition wavenumbers (in cm^{-1}) for monomers with jet-FTIR as well as other linear techniques and approximate NRI discrepancy Δ .

species	mode	NRI(F)D-IR	jet-FTIR	other	Δ/cm^{-1}
methanol	ν_{OH}	3684 ^{1,4}	3686 ¹¹	3686 ⁷	≈ 0
ethanol trans	ν_{OH}	3682 ^{2,4}	3678 ⁹	3677 ⁷	-5
ethanol gauche	ν_{OH}	3667 ^{2,4}	3661 ⁹	3660 ⁷	-7
acetic acid	ν_{OH}	3585 ^{3,4}	3585 ¹⁰		≈ 0

Table 2: Comparison of NRIDip-IR transition wavenumbers (in cm^{-1}) for dimers with jet-FTIR as well as other linear techniques and approximate NRI discrepancy Δ .

species	mode	NRI(F)D-IR	jet-FTIR	other	Δ/cm^{-1}
methanol	ν_{OH} donor	3572, ¹ 3576 ⁴	3575 ¹¹	3576, ⁷ 3574 ⁵	≈ 0
ethanol	ν_{OH} donor	3573 ^{2,4}	3547/40/32 ⁹	3548/41/32 ⁷ 3548/40/31 ¹²	+33
acetic acid	ν_{OH} ¹⁵	2930 ^{3,4}	2926 ^{13,14}		+4
	$\nu_{\text{FR}} + \nu_{\text{OO}}$ ¹⁵	2762 ^{3,4}	2748 ^{13,14}		+14
	ν'_{FR} ¹⁵	2721 ^{3,4}	2708 ^{13,14}		+13
	ν''_{FR} ¹⁵	2661 ^{3,4}	2651 ^{13,14}		+10
	ν_{FR} ¹⁵	2594 ^{3,4}	2586 ^{13,14}		+8