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Comparison of IRMPD, Ar-tagging and IRLAPS for vibrational spectroscopy of $Ag^+(CH_3OH)$

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ABSTRACT

Gas-phase $Ag^+(CH_3OH)$ molecules are produced in a laser ablation source, cooled in a supersonic expansion and their vibrational spectrum is measured by photofragment spectroscopy in a reflectron time-of-flight mass spectrometer. Three techniques – infrared multiple photon dissociation (IRMPD), argon-tagging, and infrared laser-assisted photodissociation spectroscopy (IRLAPS) – are used to measure the vibrational spectra of ions produced under identical conditions. The sharpest spectrum is obtained using IRLAPS, a two-color scheme in which a tunable OPO/OPA infrared laser excites the O–H stretch and a TEA-CO_2 laser dissociates the vibrationally excited ions via absorbing multiple C–O stretch photons. The O–H stretch is observed at 3660 cm^{-1}. Monitoring loss of argon from $Ag^+(CH_3OH)(Ar)$ gives a slightly broader peak, with no significant shift. The vibrational spectrum obtained using IRMPD is shifted to 3635 cm^{-1}, is substantially broader, and is asymmetrical, tailing to the red. Analysis of the experimental results is aided by comparison with hybrid density functional theory computed harmonic and anharmonic frequencies.

1. Introduction

Vibrational spectroscopy is widely used to measure structure and bonding of gas-phase ions [1–5]. For most ions, low ion densities preclude direct absorption studies. As a result, photofragment spectroscopy, in which absorption of light leads to fragment ion formation (and parent ion depletion) is widely used. The primary challenge in applying photofragment spectroscopy to measuring vibrational spectra is that light absorption needs to lead to bond breaking. One photon in the O–H stretching region has ~45 kJ/mol of energy, so vibrational photofragment spectroscopy requires studying weakly bound ions or absorption of multiple photons. Popular techniques for vibrational spectra of ions include infrared multiple photon dissociation, messenger spectroscopy, and two-color techniques such as vibrationally mediated photodissociation and infrared laser-assisted photodissociation spectroscopy.

Infrared multiple photon dissociation (IRMPD) can be achieved by IR radiation with high laser fluences. Photodissociation requires that the molecule sequentially absorb several photons, which provide sufficient energy to break the weakest bond, and that this energy find its way from the initially excited vibration to the dissociation coordinate. A high density of vibrational states and efficient intramolecular vibrational redistribution (IVR) facilitate IRMPD by maintaining the resonance that would otherwise be lost due to anharmonicity and by transferring energy from the vibration excited to the dissociation coordinate [6]. Small molecules such as $Ag^+(CH_3OH)$ have relatively high binding energies and low IVR rates, and are thus challenging to study via IRMPD. Despite its simplicity, IRMPD has several disadvantages. It requires high laser fluences, which can lead to spectral broadening. Multi-passing the IR beam can help to overcome this problem. A more fundamental problem is that IRMPD preferentially dissociates hot molecules, as they require fewer photons to dissociate. This leads to spectral broadening, and often to tailing of peaks to the red [7].

Messenger spectroscopy avoids many of the drawbacks of IRMPD. In messenger spectroscopy, a weakly bound atom or molecule is attached to the ion of interest. Absorption of one IR photon by the chromophore leads to loss of the messenger [8]. This allows much lower laser fluences to be used than for IRMPD. Argon is the most widely used messenger (hence the technique is often termed "argon tagging") [8–14]. Argon usually binds strongly enough that the tagged ions can be readily produced in a molecular beam source and weakly enough that absorption of one photon leads to dissociation. Vibrational resonances observed via tagging are usually sharp. This is due to the small ion-Ar binding energies, which ensure that Ar-tagged ions are relatively vibrationally cold. Usually, the tag only slightly perturbs the vibrational spectrum of the ion. However, there are some ions for which rare-gas tagging significantly perturbs the spectrum [14,15]. To check for this, it is useful to measure, and use calculations to predict, spectra with

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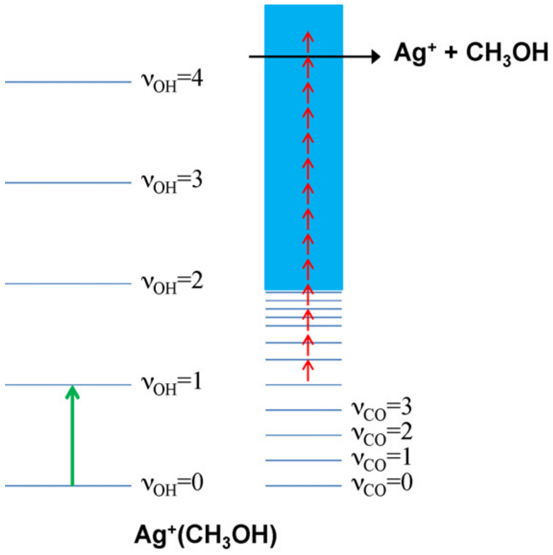

Fig. 1. Schematic representation of the two-laser infrared laser-assisted photodissociation spectroscopy of $Ag^+(CH_3OH)$. Molecules are vibrationally excited in the O–H stretching region, near 3600 cm^{-1}. Vibrationally excited molecules sequentially absorb several 929 cm^{-1} photons and dissociate.

varying number of argon atoms attached, and even to use another tag such as neon [16].

Two-color methods combine one-photon vibrational excitation with selective dissociation of vibrationally excited molecules. In vibrationally mediated photodissociation (VMP), one-photon absorption in the visible or UV promotes the vibrationally excited ions to an excited electronic state from which they dissociate [6,17–19]. This method requires that vibrationally excited molecules have a different photodissociation spectrum than the remaining, unexcited molecules. In infrared laser-assisted photodissociation spectroscopy (IRLAPS), the vibrationally excited ions absorb several photons from a second infrared laser and dissociate [20–24]. The application of IRLAPS to spectra of $Ag^+(CH_3OH)$ is shown schematically in Fig. 1. A tunable IR laser system excites the O–H stretch vibration via one-photon absorption. Vibrationally excited molecules then selectively sequentially absorb several photons in the C–O stretching region from a high-power pulsed CO_2 laser and dissociate. In principle, VMP and IRLAPS can be used to measure vibrational spectra of unperturbed ions with laser-limited resolution. These techniques require careful spatial and, in some cases, temporal overlap of both lasers with the ion cloud. In addition, one-laser background can interfere with the desired two-laser signal. Lee and coworkers first applied IRLAPS in their study of the O–H stretching vibrations of hydrated hydronium ions $H_3O^+(H_2O)_n$ ($n = 1–3$) [20]. Eyler and coworkers used a tunable, pulsed CO_2 laser to excite ions and a second, continuous wave (cw) CO_2 laser to dissociate them, measuring the spectra of $C_3F_6^+$ and $C_2H_5Cl^+$. They also quantified the two-laser signal dependence on the laser power, irradiation time, and time delay between the lasers [21]. Dopfer, Maitre and coworkers observed very low signals in IRMPD of Ag^+(phenol) using a free electron laser. Combining the free electron laser with subsequent cw CO_2 laser irradiation greatly increased the fragment ion yield, allowing them to measure the vibrational spectrum [25]. The most extensive application of IRLAPS is by Rizzo and coworkers, who have used the technique to study vibrational overtone spectra of neutral molecules such as CH_3OH and CF_3H [22,23]. In this paper, we compare vibrational spectra of $Ag^+(CH_3OH)$ obtained using IRMPD, IRLAPS and Ar-tagging. This allows us to compare the suitability of these techniques for measuring vibrational spectra of a strongly bound ion produced in a laser ablation-molecular beam source.

2. Experimental and theoretical methods

Vibrational spectra are measured using a dual time-of-flight reflectron photofragment spectrometer [26,27]. Silver cations are generated by laser ablation of a silver rod (Sigma–Aldrich, 99.8% pure). Ag^+ cations interact with a pulse of 0.5% methanol in helium or argon at a stagnation pressure of 4–5 atm. from a pulsed piezoelectric valve to produce $Ag^+(CH_3OH)$ and $Ag^+(CH_3OH)(Ar)$, respectively. Ions produced in the source expand supersonically into vacuum and cool to a rotational temperature of ~10 K [28]. Ions are accelerated to 1800 V kinetic energy, then re-referenced to ground potential before entering the field-free flight tube. Mass-selected ions are photodissociated at the turning point of the reflectron. Energetically, photodissociation of $Ag^+(CH_3OH)$ requires at least four photons in the O–H stretching region. So, vibrational spectra are obtained using infrared laser-assisted photodissociation spectroscopy (IRLAPS) and infrared multiple photon dissociation (IRMPD). In the O–H stretching region, the light source is a Nd:YAG pumped optical parametric oscillator/optical parametric amplifier (OPO/OPA, Laservision Inc.) which is tunable from 2 to 5 μm, producing ~15 mJ/pulse near 3600 cm^{-1}, with a beam diameter of 5 mm. The photodissociation efficiency is greatly improved by using a multi-pass mirror arrangement [29,30] in which light from the OPO makes 21 passes through the ion cloud. The IRLAPS experiments also use a TEA-CO_2 laser to dissociate vibrationally excited molecules via multiple photon excitation of the C–O stretch. The CO_2 laser (InfraLight SP, Optosystems, Ltd.) is line-tunable from 929.0 to 1086.8 cm^{-1}, producing up to 50–500 mJ in a 100 ns pulse, depending on the line. It makes one pass through the ion beam. The CO_2 laser beam is approximately rectangular, 4 mm × 8 mm. It is not focused. The OPO wavelength is calibrated using H_2O absorptions and CO_2 laser emission lines are calibrated using NH_3 absorptions. In the IRLAPS experiment, the OPO fires ~30 ns before the CO_2 laser. The IR beam path is purged with nitrogen to minimize absorptions by water vapor.

Fragment ions and undissociated parent ions are detected by a dual micro-channel plate detector. The ion signal is amplified, collected on a gated integrator, and averaged with a LabView based program. The photodissociation spectrum is obtained by monitoring the yield of the fragment ion of interest as a function of wavelength and normalizing to parent ion signal and laser power. In IRLAPS and IRMPD of $Ag^+(CH_3OH)$, the only fragment observed is Ag^+. As expected, photodissociation of $Ag^+(CH_3OH)(Ar)$ leads solely to loss of argon.

Computations are carried out with the Gaussian 2003 program package [31]. The optimized geometries of $Ag^+(CH_3OH)$ and $Cu^+(CH_3OH)$ are calculated using the Becke Lee–Yang–Parr hybrid HF/DFT method (B3LYP) with the SDD relativistic effective core potential and basis set on the metal and 6-311+G(d,p) basis set on the remaining atoms. Vibrational frequencies are computed to ensure that optimized geometries correspond to a local minimum. Anharmonic frequency calculations use the *opt = verytight* and *int = ultrafine* keywords. Anharmonic frequencies are not scaled. All energies include zero-point energy and correspond to 0 K values.

3. Results and discussion

The $Ag^+(CH_3OH)$ ion is a promising candidate for an IRLAPS study for several reasons. First, it is relatively small and strongly bound, so simple IRMPD is expected to be inefficient. The O–H stretch is a good IR chromophore which is also sensitive to the bonding in the molecule. The C–O stretch in bare methanol is a good IR absorber in the, rather limited, CO_2 laser tuning range. The Ag^+ cation has a $4d^{10}$, ^1S ground state. As a result, $Ag^+(CH_3OH)$ is the only stable isomer. In our calculations, we were unable to optimize an inserted [HO-Ag-CH_3]$^+$ structure; all attempts rearrange to Ag$^+$(CH_3OH). In addition, the first excited state of Ag$^+$ ($4d^95s$, ^3D) lies 470 kJ/mol above the ground state, so only singlet Ag$^+$(CH_3OH) contributes to the vibrational spectrum. This is in contrast to the iron system, where the quartet and sextet spin states of the [HO-Fe-CH_3]$^+$ and Fe$^+$(CH_3OH) isomers are at similar energies and can contribute to the spectrum, depending on how the ions are produced [7].

For bare CH_3OH, the calculated anharmonic frequencies are $\nu_{OH} = 3670\,cm^{-1}$ and $\nu_{CO} = 1015\,cm^{-1}$. These are very slightly below the experimental values $\nu_{OH} = 3681\,cm^{-1}$ and $\nu_{CO} = 1033\,cm^{-1}$ [32]. The calculations predict that Ag$^+$ binds to CH_3OH at $r_{Ag–O} = 2.21$ Å. Binding to the metal lengthens the O–H bond by 0.004 Å, to 0.965 Å and lengthens the C–O bond by 0.040 Å, to 1.464 Å. As a result, the calculated anharmonic O–H stretching frequency is predicted to drop to $3644\,cm^{-1}$ and the C–O stretching frequency drops to $927\,cm^{-1}$. This is slightly below the $929\,cm^{-1}$ lower limit of our CO_2 laser. The calculated Ag$^+$-CH_3OH dissociation energy is 145 kJ/mol. Thus, for IRMPD in the O–H stretching region, at least four photons are required to break the bond. Using the CO_2 laser alone, 13 photons need to be absorbed to dissociate the molecule. In the IRLAPS experiment, after absorbing one photon in the O–H stretch region, dissociation requires 9 additional CO_2 photons.

3.1. *IRLAPS of Ag$^+$(CH_3OH)*

We measure and compare the vibrational spectra of Ag$^+$(CH_3OH) molecules obtained using three techniques: IRLAPS, IRMPD, and argon-tagging. In infrared laser-assisted photodissociation spectroscopy (IRLAPS) one vibrationally excites the molecules using a tunable laser. Vibrationally excited molecules are then selectively photodissociated using a high-power laser such as a CO_2 laser (Fig. 1). Ideally, the molecules are vibrationally excited to an energy where the density of vibrational states is sufficiently high that they form a quasi-continuum, and they absorb CO_2 laser photons much more readily than vibrationally unexcited molecules. In this ideal case, fragmentation is only observed when both lasers are present, and there is no background from either laser alone. This has been observed in studies by Rizzo and coworkers, where it is achieved by exciting vibrational overtones, so that one reaches the quasi-continuum, even for small molecules [22,23,33]. Background from the CO_2 laser is minimized by tuning the CO_2 laser to the red of the resonant absorption for vibrationally unexcited molecules and decreasing the CO_2 laser power until it induces negligible dissociation alone. Vibrational absorptions are shifted to the red for vibrationally excited molecules due to vibrational cross-anharmonicities [33].

Fig. 2 shows the IRLAPS spectrum of the O–H stretching fundamental in Ag$^+$(CH_3OH). This is obtained with 50 mJ/pulse at the 10P(36) CO_2 laser transition, at $929.0\,cm^{-1}$, and with ~16 mJ/pulse at $3600–3700\,cm^{-1}$. In this experiment, there is significant one-laser background. Each laser dissociates ~4% of the ions. As a result, we measure the normalized fragment ion yield with both lasers on (brown trace, top) and subtract from it the fragment yield measured from each laser alone (green trace, middle). The result is the IRLAPS spectrum, shown in blue, bottom. It consists of a slightly asymmetric peak at $3660\,cm^{-1}$, with full-width half-max (FWHM) of $50\,cm^{-1}$. The anharmonic calculations predict an O–H stretching frequency of $3644\,cm^{-1}$, in good agreement with our experimental result.

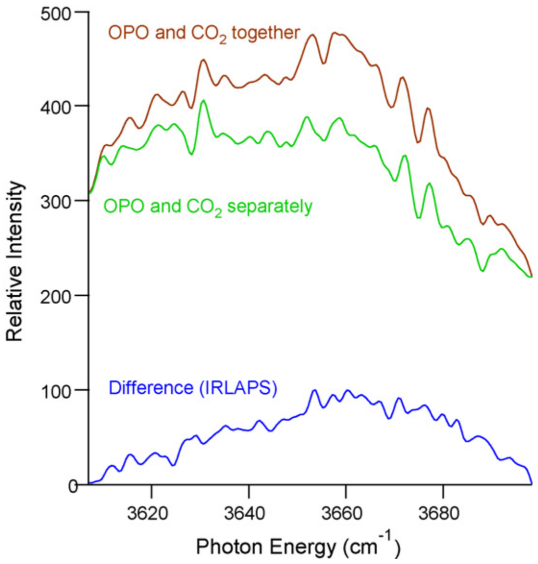

Fig. 2. IRLAPS spectrum of Ag$^+$(CH_3OH) in the O–H stretching region. In addition to the two-color signal, there is significant one-color background. This background is shown in the green trace, which is the sum of the Ag$^+$ fragment yield, normalized to laser power, from the CO_2 laser (which is not scanned) alone and from IRMPD by the tunable OPO alone. The brown trace shows the normalized signal with both lasers on. The enhanced dissociation yield (the difference between the brown and green traces) is the net IRLAPS signal, and is shown in blue. The dips in the spectra are due to loss of laser power due to absorption by trace atmospheric water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In order to optimize the signal to background in the IRLAPS experiment, we measured the dependence of the one-laser background and two-laser signal on the OPO and CO_2 laser power and CO_2 laser wavelength. The one-laser IRMPD background and two-laser IRLAPS signal were measured at OPO/OPA laser powers of 5–16 mJ/pulse and CO_2 laser powers of 25–50 mJ/pulse. The IRMPD fragment yield depends on (OPO laser power)$^{1.7}$ or on (CO_2 laser power)$^{1.9}$. The IRLAPS signal depends linearly on the OPO laser power and depends on (CO_2 laser power)$^{1.6}$. As expected, IRLAPS is favored at lower power from each laser, but the effect is small. This is in contrast to power dependencies measured by Rizzo and coworkers in IRLAPS studies of methanol overtones, where the threshold for IRLAPS is significantly lower than that for IRMPD [24]. As a result, they were able to select laser powers at which they could obtain reasonable IRLAPS signal with negligible one-color background. There are two likely reasons for our having to use such high CO_2 laser power: the choice of CO_2 laser wavenumber, and whether the vibrationally excited molecule is in the quasi-continuum region. To optimize IRLAPS signal and minimize CO_2 laser background, Rizzo and coworkers tune the CO_2 laser to the red of the transition in the vibrationally unexcited molecule. The anharmonic calculations predict that the C–O stretch in Ag$^+$(CH_3OH) lies at $927\,cm^{-1}$. We find that the fragment ion yield for both IRLAPS and IRMPD improves with decreasing CO_2 laser wavenumber. The $929\,cm^{-1}$ transition used is the lowest available for our laser. Unfortunately, the limited tuning range of the CO_2 laser does not allow us to explore wavenumbers significantly to the red of the C–O stretch. We also tried to measure ν_{OH} in Cu$^+$(CH_3OH) via IRLAPS. Although each laser produced photofragments, no net IRLAPS signal was observed. The anharmonic frequency calculations predict $\nu_{CO} = 908\,cm^{-1}$ in Cu$^+$(CH_3OH), significantly lower than the value in Ag$^+$(CH_3OH), and well below the CO_2 laser tuning range. Large red-shifts in ν_{CO} upon binding to metal cations have also been quantified by Dietrich et al. for $Au_n^+(CH_3OH)_m$ using IRMPD with a CO_2 laser [34]. Clusters with fewer methanol molecules show progressively larger red-shifts. The C–O stretch frequency lies below $929\,cm^{-1}$ even for Au$^+$(CH_3OH)$_2$.

Rizzo and coworkers also observe that the threshold CO_2 laser power required for IRLAPS is lower for more highly vibrationally excited CH_3OH. This is a result of the steep increase in vibrational

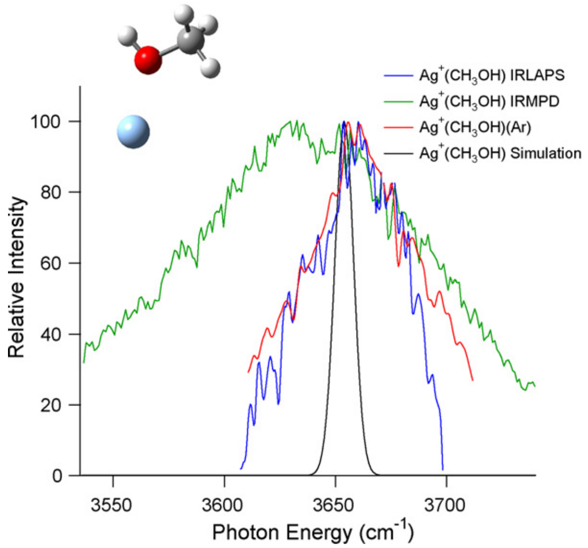

Fig. 3. Comparison of vibrational spectra of $Ag^+(CH_3OH)$ in the O–H stretching region. The spectra obtained using IRLAPS (blue) and argon-tagging (red) are similar. The IRMPD spectrum is significantly broader, especially to lower wavenumber.

density of states ρ_{vib} with increasing internal energy. At higher initial vibrational energies, the molecules are more likely to be in the quasi-continuum region and to sequentially absorb CO_2 laser photons more readily. Also, fewer CO_2 photons are required to dissociate the molecule. For $Ag^+(CH_3OH)$, we calculate that $\rho_{vib} = 50$ states/cm^{-1} at $\nu_{OH} = 1$. This is not quite in the quasi-continuum, and may make CO_2 laser absorption less efficient. This effect was also noted by Lee and coworkers in their study of $H_3O^+(H_2O)_n$. For $H_5O_2{}^+$, at $\nu_{OH} = 1$, ρ_{vib} is only 38 states/cm^{-1}, so they observe less efficient absorption of CO_2 photons than for $H_7O_3{}^+$ and $H_9O_4{}^+$, which have much higher densities of states at the same energy [8]. In summary, both conditions – not tuning significantly to the red of ν_{CO} in the unexcited molecule and the low density of states at $\nu_{OH} = 1$ – are responsible for the significant one-color background.

3.2. *IRMPD of $Ag^+(CH_3OH)$*

In the O–H stretching region, IRMPD of $Ag^+(CH_3OH)$ requires at least four photons. Using the multi-pass mirror arrangement, we observe ∼4% dissociation near 3635 cm^{-1}. The only fragment observed is Ag^+. The IRMPD spectrum is shown in Fig. 3 (green trace). It consists of a peak at 3635 cm^{-1}, with a width of 180 cm^{-1}. This is 25 cm^{-1} red-shifted and significantly broader than the peak observed using IRLAPS. The O–H stretches of several other $M^+(CH_3OH)$ systems have also been measured using IRMPD. Those spectra show similarly broad features. Weinheimer and Lisy [35] observe a peak at 3663 cm^{-1} (108 cm^{-1} FWHM) for $Cs^+(CH_3OH)$. For $Mg^+(CH_3OH)$, Machinaga et al. [36] obtain a 200 cm^{-1} wide peak at 3520 cm^{-1}, and Furuya et al. measure a 130 cm^{-1} wide peak at 3490 cm^{-1} for $Al^+(CH_3OH)$ [12].

3.3. *Argon-tagged $Ag^+(CH_3OH)$*

Photodissociation of $Ag^+(CH_3OH)(Ar)$ provides another means to measure the O–H stretching frequency. The computed argon binding energy is 24 kJ/mol (2000 cm^{-1}), so one photon in the O–H stretching region can break the bond. Ar-tagging is calculated to blue-shift the O–H stretching frequency by 3 cm^{-1}. Experimentally, loss of argon is the only photodissociation fragment observed. The resulting photodissociation spectrum is shown in red in Fig. 3. It consists of a peak at 3660 $cm^{-1}$with a width of 60 cm^{-1}. This is narrower than the IRMPD spectrum, but is slightly broader than that obtained by IRLAPS. There is no significant shift between the Ar-tagging and IRLAPS spectra. The photodissociation spectrum of $Ag^+(CH_3OH)(Ar)$ is broader than is typically observed for Ar-tagged ions. Much of the width of the Ar-tagged and IRLAPS spectra is likely due to sequence bands from vibrationally excited ions. Attachment of Ag^+ to CH_3OH is 145 kJ/mol exothermic. Ideally, collisions with the carrier gas in the ablation source and subsequent expansion remove this energy. However, molecular beams cool vibrations much less efficiently than rotations. As a result, the $Ag^+(CH_3OH)$ can be vibrationally excited, particularly in the low-frequency intermolecular vibrations and CH_3OH torsion. A similar effect is expected for $Ag^+(CH_3OH)(Ar)$, except the 2000 cm^{-1} Ar binding energy limits the vibrational energy.

Several groups have measured the O–H stretching frequencies of $M^+(CH_3OH)$ complexes using IRMPD and Ar-tagging. Binding to the metal lowers ν_{OH} from its value in bare methanol (3681 cm^{-1}). For many metals, this red-shift is small. For example, Weinheimer and Lisy measure $\nu_{OH} = 3663$ cm^{-1} in $Cs^+(CH_3OH)$ [35], and 3659 cm^{-1} in $Na^+(CH_3OH)_2$ (the value for $Na^+(CH_3OH)$ is likely to be similar, as there is little shift in going from $Na^+(CH_3OH)_n$, $n = 4–2$) [37]. We measure $\nu_{OH} = 3660$ cm^{-1} in $Ag^+(CH_3OH)$. Previously, we observed $\nu_{OH} = 3630$ cm^{-1} in $Fe^+(CH_3OH)$ via Ar-tagging [7]. Hirabayashi et al. measured O–H stretches for $Ni_n{}^+(CH_3OH)$, obtaining $\nu_{OH} = 3634$ cm^{-1} for $n = 3$ and 3645 cm^{-1} for $n = 4$ [38]. They measure similar values for $Co_n{}^+(CH_3OH)$ [39]. There are two metals which give much larger red-shifts. For $Mg^+(CH_3OH)$, Machinaga et al. measure a broad peak at 3520 cm^{-1} using IRMPD and a much narrower peak at 3560 cm^{-1} using Ar-tagging [36]. $Al^+(CH_3OH)$ shows a further red-shift, to $\nu_{OH} = 3490$ (IRMPD) and $\nu_{OH} = 3495$ (Ar-tagged), as measured by Furuya et al. [12].

4. Summary and conclusions

IRLAPS gives the narrowest vibrational spectrum of $Ag^+(CH_3OH)$ in the O–H stretching region. The spectrum obtained via Ar-tagging is slightly broader and shows no significant shift. In contrast, IRMPD leads to a peak that is three times as broad, is 25 cm^{-1} shifted to the red, and which exhibits significant tailing to the red. With the same laser ablation source, for larger molecules, we find that IRMPD can give narrower peaks. For example, IRMPD of Fe^+(phenol) gives a peak at 3598 cm^{-1}, with 45 cm^{-1} FWHM [30]. This is despite the fact that Fe^+(phenol) is more strongly bound than $Fe^+(CH_3OH)$. The narrower spectrum is likely due to the greater IVR rate in Fe^+(phenol), which allows for efficient sequential multiple photon absorption by rapidly transferring energy out of the O–H stretch vibration. This also suggests that IRLAPS may be more efficient and give narrower features for larger molecules, as one O–H quantum is sufficient to reach the quasi-continuum region, facilitating subsequent absorption of CO_2 laser photons.

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